LABORATORY EVALUATION OF ACID DIVERSION BY VISCOELASTIC SURFACTANT IN CARBONATE RESERVOIRS

BY

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DEDICATED TO

MY LOVING FATHER, MOTHER, WIFE,

BROTHERS AND SISTERS

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THESIS ABSTRACT

NAME: Msalli Awadh Al-Otaibi

TITLE: Laboratory Evaluation of Acid Diversion by Viscoelastic Surfactant in Carbonate Reservoirs

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Acid stimulation treatments are achieved by creating long wormholes inside the reservoir formation which results in increasing the productivity of the reservoir. Viscoelastic surfactants (VES) have been introduced in the industry to offer effective and uniform stimulation treatments. Customizing acid VES based treatments to field's applications is a key factor to the success of the stimulation treatment. The treatment design parameters include water salinity, additives, and diverting agent concentration. Also, the targeted reservoir section permeability contrast is a major parameter for the success of the treatment application.

These parameters need to be evaluated and optimized to ensure an efficient diversion of the acid stimulation treatment. The diversion efficiency of the acid VES based system and the effect of different parameters on the diversion efficiency of the VES system and its viscosity in spent and live acid were studied. The effect of permeability contrast on the diversion efficiency of 15% HCl VES based treatment was investigated in parallel core flooding equipment. Samples with high and low permeability contrasts were used in the core flooding experiments with a range of 0.7-56.25 mD. The effect of water salinity on VES viscosity and diversion efficiency was evaluated using distilled water, field water, and seawater. Also, the effect of VES concentration on the diversion efficiency of the treatment fluid and its viscosity was

studied over 1 - 7.5 vol.%. The temperature effect on the viscosity and diversion efficiency of the VES system was evaluated.

The results and conclusions drawn from this research provided for the first time experimental evidence of the diversion efficiency of the VES system using long carbonate core samples through return permeability results. Also, it showed the impact of the different parameters studied on the diversion efficiency of the VES and how they can be modified to increase the efficiency of carbonate acid stimulation treatments. The results also showed strong relationship between the viscosity and the diversion efficiency of the acid VES based system. These results provided basis for future studies on the rheology and diversion efficiency of the acid VES based system.

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ملخص البحث

الاســـــــــم: مسلي عوض العتيبي

عنـوان الرساله: دراسة مخبريه لكفائة الفيسكو الاستك سرفاكتنت مع الحمض في تحفيز انتاج مكامن النفط

التـخـصـــص: هندسة كيميائيه

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عمليات التحفيز بأستخدام الاحماض تتم على نطاق واسع في صناعة النفط و الغاز لتعزيز إنتاجية آبار النفط والغاز و كذلك آبار الحقن بالمياه. يتم تحقيق تحفيز طبقات مكامن الكربونات من خلال خلق ثقوب طويلة داخل المكامن والتي تزيد من النفاذيه هذه المكامن. عادة, النفاذيه في مكامن النفط و الغاز تكون مختلفه بشكل كبير من جزء الى اخر و التي تزيد من صعوبة التوصل الى نجاح عملية التحفيز. و قد ادخلت ماده لزجه تسمى فيسكو الاستك سرفاكتنت للتغلب على هذا التحدي و تحقيق التحفيز الفعال لمكامن النفط و الغاز. جزيئات هذيه المواد تشكل حلقات كبيرة الحجم نسبيا مع وجود الملح و ارتفاع درجة الحموضة (الرقم الهيدروجيني> ٢) و الذي ينتج في زيادة لزوجة السائل بشكل كبير. تصميم مكونات المواد الحمضيه بالاضافه الى الماده اللزجه يعتمد على التطبيقات الميدانية.

تصميم هذي المواد و تكوينها بطريقه فاعله يعتبر عامل رئيسي في نجاح العمليات التحفيزيه لمكامن النفط. عملية التصميم تشمل ملوحة المياه المستخدمه و تركيز الماده اللزجه و المواد الاخرى المضافه. بالاضافه الى تصميم المواد, نفاذية الجزء المستهدف من مكامن النفط هو كذلك عامل رئيسي لنجاح تطبيق العلاج التحفيزي. هذه العوامل يجب دراسة تأثيرها على تحفيز الانتاج و تصميم تركيزها في العلاجات الحضميه لضمان نجاح عملية تحفيز الانتاج. أطروحة الماجستير تدرس كفائة المواد اللزجه في تحقيق تحفيز الانتاج في مناطق المكامن ذات النفاذيه العاليه و القليله. كذلك البحث يدرس تأثير العوامل المختلفة على كفاءة المواد اللزجه في عمليات التحفيز. لتحقيق اهداف البحث, تم استخدام عينات من صخور المكامن على درجات مختلفه من النفاذيه و كذالك تم استخدام تركيز ١% و ٣.٧٥% و ٧.٥ % في دراسة تأثير تركيز الماده اللجزه على التحفيز. و كذلك تم استخدام عينات من المياه المقطره, مياه البحر, و مياه تستخدم في عمليات التحفيز في الميدان. تأثير درجة حرارة المكامن على كفائة المواد اللزجه تم دارسته باستخدام دراجات حراره مختلفه.

نتائج البحث تمثل و للمره الاولى باستخدام النفاذيه كدليل اثبات على كفائة المواد اللزجه على تحفيز الانتاج في عينات صخيره ذات نفاذيه متفاوته. كذلك النتائج أثبتت أن كفائة الفيسكو الاستك سرفاكتنت تعتمد اعتماد كبير على درجة الحراره, نسبة الفيسكو الاستك سرفاكتنت في المواد الحمضيه, تركيز الاملاح المضافه, و كذلك درجة اختلاف النفاذيه في المكامن. وأثبتت الدراسه ان العوامل اللتي تمت دراستها يمكن تصميمها لزيادة كفائه الفيسكو الاستك سرفاكتنت لتحفيز انتاج النفط و الغاز باستخدام المواد الحمضيه. أظهرت نتائج البحث أيضا علاقة قوية بين لزوجة المواد الحمضيه بوجود الفيسكو الاستك سرفاكتنت وكفاءة التحفيز. قدمت هذه النتائج أساسا لدراسات مستقبلية على الريولوجيا وكفاءة الفيسكو الاستك سرفاكتنت.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول و المعادن

المملكة العربيه السعوديه – الظهران - 31261

CHAPTER ONE

INTRODUCTION

1.1 Acid Stimulation Treatments

Acid stimulation treatments are widely conducted in the oil industry to enhance productivity of oil and gas wells. They are also applied to increase water injectivity of water injections wells. The objective of acid stimulation is achieved by creating new channels and wormholes inside the carbonate reservoir formation8. These wormholes and channels are created deep inside the formation to increase the reservoir permeability and connectivity and to allow for more fluid flow. Another objective of acid stimulation is to remove and bypass formation damage caused by drilling and completion operations and drilling fluid particles (Al-Ghamdi et al., 2009).

Acid stimulation treatments are different in composition and formulations depending on the type of targeted reservoir formation. For carbonate reservoir type formations, acid is injected in the formation below fracture pressure to avoid fracturing the reservoir and losing the treatment fluid. Once the injected acid comes in contact with the carbonate rock, it reacts and dissolves the carbonate rock minerals, $CaCO_3$ and $CaMg(CO_3)_2$ (Nasr-El-Din et al., 2007).

The reaction between the carbonate rock and the acid fluid is relatively simple due to the composition of carbonate formation and temperature. Carbonate reservoir formation is composed of calcium carbonate ($CaCO_3$) and/or dolomite ($CaMg(CO_3)_2$).

formation is composed of calcium carbonate ($CaCO_3$) and/or dolomite ($CaMg(CO_3)_2$). These formation components are highly reactive to acids. For example, 7.5 wt.% citric acid , which is weaker than the most common used acid (HCl) in well acid stimulation, has an acid reaction rate of 9.5 X 10^{-7} mol/cm^2/s with $CaCO_3$ at 50 ^oC (Alkhaldi et A., 2009).

The governing chemical reaction equations of both rocks, calcium carbonate ($CaCO_3$) and $CaMg(CO_3)_2$, with the hydrochloric acid are shown in Equations 1 and 2.

$$2\,HCl + CaCO_3 \quad ====> \quad CaCl_2 + CO_2 + H_2O \qquad \text{Equation-1}$$

$$2\,HCl + CaMg(CO_3)_2 \quad ====> \quad CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O \qquad \text{Equation-2}$$

Both reactions result in generation of $CaCl_2$, $MgCl_2$, CO_2, and water. These reaction products have high solubility in the spent hydrochloric solution. Calcium chloride particles have a solubility of 74.5 g/100mL in the spent HCl acid. The generation of these salts in the spent acid increases the salinity of the solution. The salts' high solubility makes it possible for the treatment to achieve its objectives without leaving precipitation behind. The precipitation while stimulation is highly undesirable to eliminate the risk of formation damage and reduction of permeability.

Achieving effective stimulation of long horizontal wells with intervals lengths ranging from 3,000 to 5,000 feet is a challenging task. The challenge behind effectively stimulating these wells arises due to mainly the high reactivity of the acid to the carbonate reservoir rock, the drastic permeability contrast, and the high length of the

targeted interval. If this challenge is not addressed in the treatment program, the acid treatment will flow into the most permeable zones or the least resistance path leaving long intervals of the targeted section untreated (Nasr-El-Din et al., 2007).

1.2 Acid Diversion Systems

Acid diversion is utilized to address the challenge of stimulating long horizontal wells to achieve effective stimulation and high productivity and injectivity. In fact, effective diversion is considered a key factor for the success of the matrix acidizing of carbonate reservoirs. Acid diversion is classified into two main types, mechanical diversion and chemical diversion. Each of these types has different techniques. Generally, chemical techniques are preferred due to the low cost involved and fewer stages required to achieve acid diversion. However, there are other determining factors behind applying the diversion technique such as the well completion type, targeted efficiency, well condition, and economic considerations (Safwat et al., 2002).

1.2.1 Mechanical Diversion

Mechanical diversion utilizes mechanical means to divert the acid treatment from high to low permeable zones in efforts to achieve effective acid stimulation of the targeted reservoir interval. This is accomplished through isolating different zones while placing the stimulation treatment fluid. For open hole completions, packers are used for mechanical diversion where for cased and perforated completions, ball sealers are used for diversions. Also, coiled tubing techniques are used as means of mechanical diversion (Chang et al., 2007).

Efficiency of mechanical diversion has been studied and found to be dependent on different parameters. Ball sealers efficiency relies heavily on parameters such as roundness and smoothness of the perforation holes, degradation of the ball sealers and flow rate. A disadvantage of coiled tubing is the limitation on the maximum achievable flow rate that can be applied while placing the acid fluid which is a key parameter in the treatment success. The limitation of the maximum flow rate is due to the small diameter of the coiled tubing. Also, coiled tubing has limitations in the maximum achievable reach which requires special tools to reach long horizontal sections such as tractors or vibrators (Chang et al., 2007).

1.2.2 Chemical Diversion

A. Foam

Foams have been used for diversion purposes in the oil industry for more than 40 years. They are generated by adding a surfactant to the acid treatment and using the treatment fluid as the continuous phase and a gas as the non-continuous phase. The two phases are mixed with high mixing force in a porous medium to create the foam. This diversion technique depends on the foam resistance to flow once it is inside the formation. The foam resistance creates a high pressure drop which diverts the treatment fluid to flow to other untreated sections. The main advantage of foam diversion technique is that it does not contain solids or polymers that could damage the reservoir formation and reduce permeability. However, foams have a disadvantage of a short life-time and can be relatively unstable especially in the presence of hydrocarbons such as crude oil (Chang et al., 2007).

Foams can be stabilized by the addition of water-soluble polymer such as xanthan, cellulose, or guar. These polymers have different stability effects as shown in **TABLE 1.1**. Also, the polymer concentration in the foam has a proportional effect on the stability of the foam as shown in **TABLE 1.1**. Although the addition of water-soluble polymer stabilizes the foam, adding a polymer in the treatment fluid has a negative effect as it may cause formation damaging and reduce reservoir permeability. Once the added polymer enters the formation and cause reduction in the permeability, an additional treatment will be required to remove the polymer damage effect. In many cases, using a treatment to remove the trapped polymers may not be sufficient. A recent study showed a maximum of 50% of the trapped polymer can be retained (Safwat et al., 2002).

TABLE 1.1: Stability (half-life time in minutes) of conventional foam containing various polymers. In the time indicated, 50% of the fluid will be drained. [Safwat et al., 2002]

Polymer Type	**Polymer Loading, ptt**		
	20	30	40
Xanthan	75	190	440
Cellulose	16	26	51
Guar	14	20	40
HPG	7	14	27

B. Emulsified Acid

HCl acid is very reactive with carbonate reservoir rock and therefore, it does not penetrate to sufficient depths in the reservoir. Emulsified acid is used to ensure deep penetration of the acid deep inside the formation and lower the acid consumption in the higher permeable zones. Emulsified acid is prepared by using an emulsifier to make the diesel to be the emulsion external phase and the hydrochloric acid to be the internal phase with usually a ratio of 70:30 by volume. This technique showed high efficiency in achieving high penetration inside the formation. The emulsified acid was evaluated by a recent study. The study used a core flood system, a carbonate sample and two types of fluids, regular acid treatment and emulsified acid. A constant amount of each treatment fluid was injected into two identical core samples and then the penetration depth was measured. The results are shown in **Figure 1.1** (Safwat et al., 2002).

The results show that the live acid resulted in shorter penetration inside the core sample where the emulsified acid achieved longer penetration depth. The live acid fluid was consumed as it reached the carbonate sample because there was a direct contact between the acid and the calcium carbonate particles. In the other treatment, the acid was coated with diesel which resulted in reducing the contact time between the acid and the carbonate rock which resulted in less consumption of acid at the beginning and longer penetration depth. Although emulsified acid showed longer penetration inside the formation, it is not effective to divert acids from high permeable zones to lower permeable zone to achieve stimulation of the total targeted reservoir interval (Safwat et al., 2002).

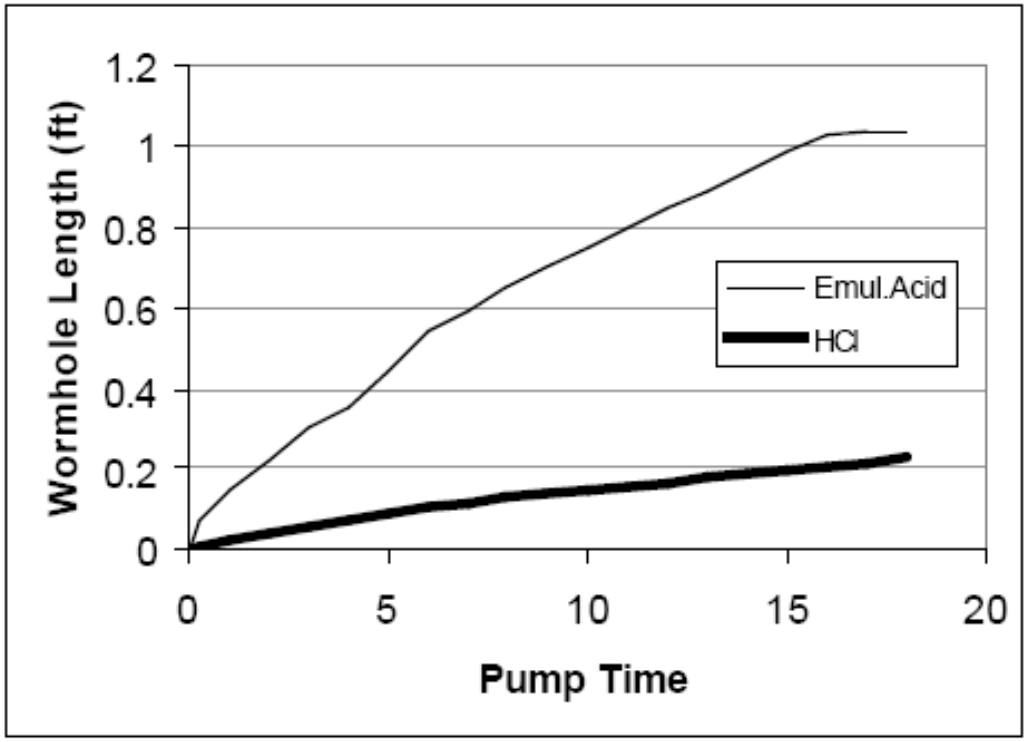

Figure 1.1: Penetration length of regular and emulsified acids at 20 wt. % HCl. [Safwat et al., 2002]

C. Polymer-Based Diverted Acid

Polymers have been used in the oil industry for decades as diverting agents. The polymers are added to the acid treatment to increase its viscosity which will help in diverting the acid treatment from high permeable zones to lower permeable zones. Polymer-based viscous acid treatments achieve the diversion by reducing the acid flow inside the high permeable zones through the viscosity effect of the treatment and the polymer plugging. This will allow the rest of the treatment fluid to be diverted and injected to the other interval sections (Nasr-El-Din et al., 2004).

Polymer based acid treatments were evaluated in the lab where they showed high diversion efficiency. However, it was found that they have a damaging effect to the

reservoir formation. That is attributed to the polymers present in the treatment which will be trapped inside the formation after the treatment penetrates inside the reservoir. The polymer usually gets trapped and results in a reduction in the formation permeability (Nasr-El-Din et al., 2004).

D. Visco-Elastic Surfactant (VES) Diverted Acid

Viscoelastic surfactants have been used in the oil industry in the past few years as diverting additives for acid treatments. This is attributed to their ability to significantly increase the acid viscosity. Acid VES-based systems are polymer-free and solids-free systems; this feature makes them non-damaging compared to other chemical diverting techniques (Nasr-El-Din et al., 2004). The viscosity of VES systems is gained from the interaction between the acid reaction products (salts) and the viscoelastic surfactant molecules. With the rise of pH value above 2 and the increase in the concentration of the divalent cations (Ca^{2+} and Mg^{2+}) in the spent acid, the visco-elastic surfactants molecules form long worm-like micelles which cause the viscosity of the treatment fluid to increase dramatically. The increase in viscosity is function of the concentration of the generated salts and the pH of the solution. **Figure 1.2** shows the mechanism of making and breaking the viscoelastic surfactants (Chang et al., 2001).

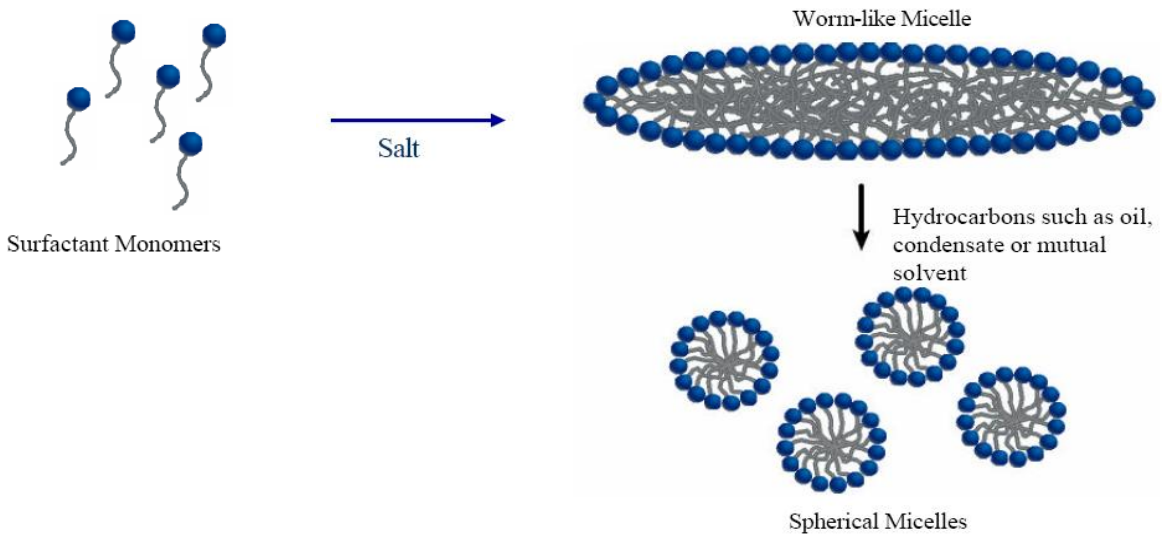

Figure 1.2: The mechanism of making & breaking of viscoelastic surfactnats. [Safwat et al., 2002]

VES-based divergent acid system has a water-like viscosity on the surface and in the wellbore but its viscosity increases significantly when it penetrates inside the carbonate reservoir formation rock. The viscosity is generated inside the formation as the acid component of the treatment reacts with the reservoir rock and generates salts. This increase in viscosity inside the reservoir matrix will create high pressure buildup resulting in slowing the treatment flow in the high permeability zones and, therefore, diverting the treatment flow to the lower permeability zones. In contrast to the VES-based diverted system, polymer-based diverted system is already viscous on surface and requires high pump pressure to pump the treatment at high desirable flow rate (Nasr-El-Din et al., 2008).

The high viscosity of the spent acid can be reduced and the well can be cleaned up after the treatment is completed by either hydrocarbons contact during flow back or injection of solvent. For water wells, solvents or mutual solvents can be used to break the viscosity of the treatment inside the formation. After the cleanup, the VES does

not leave a residue in the formation as it will break into very small spheres-shaped surfactants (4-10 nm in diameter) which can be easily flown back from the formation porous medium to the surface (Chang et al., 2001).

Field results have shown the success of VES when used as a diverting system in acid stimulations. VES has shown higher efficiency than other conventional acid-diverted systems. Oil production was compared in a field treated with conventional acid treatment and VES based acid treatment. An average of 1,600% more production resulted from wells treated with VES systems. In another field data, it was shown that VES divergent technique resulted in a 4 to 5 folds increase in oil production compared to conventional methods. Due to the low volume required in VES-based treatments compared to polymer-based systems, VES is attractive from operational perspective in off-shore environments where tanks and other logistic aspects are critical (Chang et al., 2007).

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction to Viscoelastic Surfactant

Surfactants in general contain two functional groups, hydrophilic and hydrophobic groups. The hydrophilic group is the polar group which forms hydrogen bond with water and becomes water-soluble. The hydrophobic group is non-polar and hydrocarbon-soluble. The hydrophobic group is usually a long hydrocarbon chain. The hydrophilic group, on the other hand, is formed by moieties such as carboxylates, sulfates, sulfonates (anionic), alcohols, polyoxyethylenated chains (nonionic) and quaternary ammonium salts (cationic). Surfactants have a wide range of applications in pharmaceutical, food, detergency, agriculture, paint, paper, ceramic and petroleum industries (Holmberg et al., 2002 and Schramm et al., 2000).

There are five major types of surfactants that include anionic, cationic, nonionic, zwitterionic and amphoteric. The polar head group of the surfactant determines the type of the surfactant. The surfactants that contain at least one negative and one positive charge are called zwitterionic surfactants. Amphoteric surfactants, on the other hand, are substances which can have anionic, cationic, or zwitterionic properties at different pH values. At an acidic pH, the amphoteric surfactant molecules will be protonated to form cations, while at an alkaline pH they will be deprotonated to form anionic species. At mid-pH range, amphoteric surfactants exist as neutral molecules,

zwitterionic characteristics. **Figure 2.1** shows the amphoteric and zwitterionic behavior at different pH values (Holmberg et al., 2002).

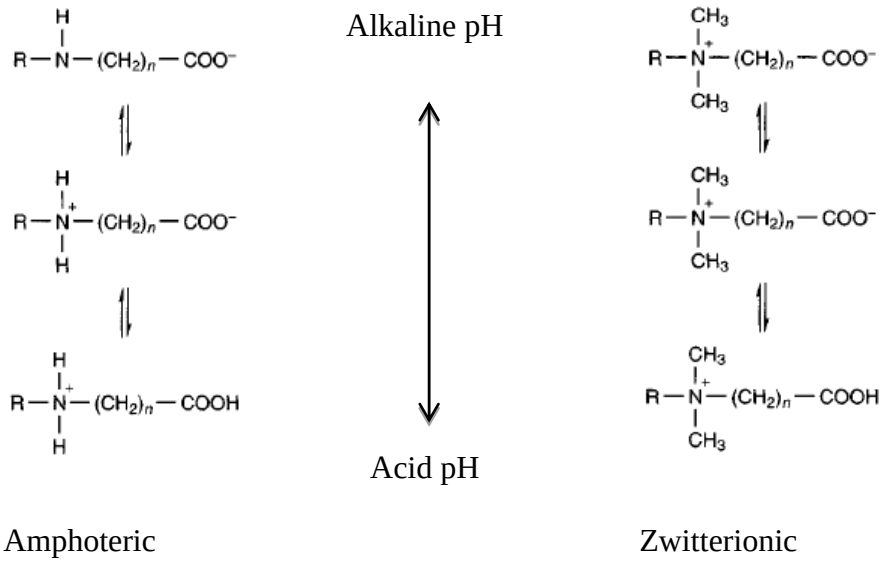

Figure 2.1: Amphoteric and Zwitterionic surfactants with different pH [from Holmberg et al., 2002]

The other two types of surfactants are anionic and cationic surfactants. The cationic surfactants have a positive charge on the polar group while the anionic surfactants have a negative charge on the polar group. These two types of surfactants have lower tolerance to electrolytes and salts because of their high chemical interaction. This fact makes zwitterionic surfactants are preferred for acid stimulations jobs (Daniel et al., 2002). Viscoelastic surfactants are types of surfactant which exhibit the ability to align themselves and form wormlike micelles in the presence of salts. This feature results in increasing the viscosity of the VES-based acid significantly. It was noticed that the viscosity is function of pH; the higher the pH, the more viscous is the solution. In general, the viscosity increases dramatically with salt concentration at pH above 2 (Chang et al., 2001).

2.2 VES Gelling Mechanism

The viscosity of VES solution develops as a result of the presence of salts such as $CaCl_2$ in the solution and the increase of the pH. This happens when the acid reacts with calcium carbonate rock to produce $CaCl_2$ as shown in Equation 1. This scenario takes place when VES acidic system is applied in the wellbore, across the carbonate reservoir rock formation which contains $CaCO_3$ particles, sometimes 95% $CaCO_3$. The result of the acid reaction with the calcium carbonate particles increases the solution pH and the concentrations of cations, Ca^{2+} and Mg^{2+}. These two resulting products force the surfactant molecules to align as shown in **Figure 1.2** and form rod-like structure (Nasr-El-Din et al., 2008).

The resulting shape of the surfactant molecules increases the viscosity of the solution due to the long rod-like structures which entangle and hinder the fluid movement. The increase in viscosity slows the fluid flow through the higher permeability zones which receives more treatment fluid at the beginning. With more reaction and increase in the viscosity, this zone will be blocked and no more fluid will be allowed to penetrate further. This restriction in fluid movement in the high permeable zones forces the treatment flow to divert to other zones where the permeability is low. (Nasr-El-Din et al., 2008).

The worm-like structures are stable in aqueous environment, hence maintaining the fluid viscosity in water-containing formations. The high viscosity of the VES acid system can be lowered significantly by the addition of a hydrocarbon phase. This is achieved when the rigid worm-like micelles are disrupted to form very small spherical structures (4-10 nm) when exposed to hydrocarbons as shown in **Figure 2.2**

(Holmberg et al., 2002). After the viscosity is reduced and the rod-like micelles are broken, no residuals remain after the material degradation (Chang et al., 1999). For oil producer wells, the viscosity breaking of VES system can be achieved by flowing back oil well after the treatment application. For an injector well or a dry gas producer, solvent or mutual solvent is injected in the formation to break the VES viscous fluid (McCarthy et al., 2002). **Figure 2.2** illustrates how the surfactants react with the acid spending after acid reaction with the rock formation and how the viscous fluid is broken when hydrocarbon gets into contact with VES system, with the well flow back (Nasr-El-Din et al., 2008).

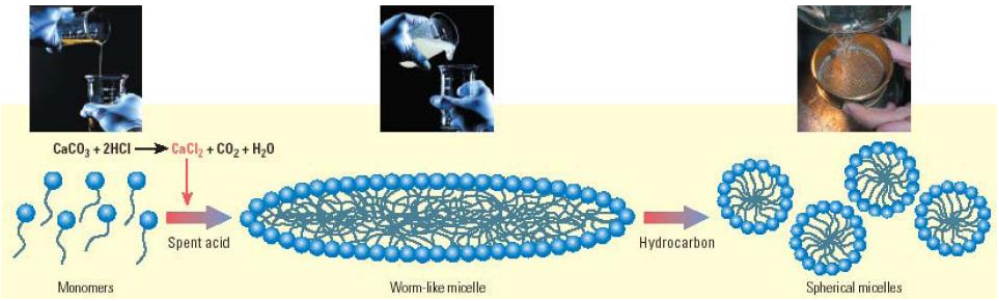

Figure 2.2: Illustration of VES structural changes due to acid spending and reaction with hydrocarbons [Nasr-El-Din et al., 2008]

2.3 Rheology Studies

Recent studies have shown that VES-based acid system rheology is dependent on several parameters. These parameters include acid concentration, temperature, dissolved salts concentration, pH, additives, salinity of mixing water, shear rate, and mixing procedure. As these parameters have impact on VES rheology, they are expected to have an effect on the diversion efficiency. The following sections demonstrate the previous research work conducted on the effects of these parameters on VES acid systems (Nasr-El-Din et al., 2007).

2.3.1 Effect of Temperature on VES-based acid Viscosity

The temperature effect on VES rheology was studied over a wide range of temperatures and using different types of viscoelastic surfactants. There was a consistent trend of viscosity change as function of temperature for different VES surfactants. The viscosity was noticed to increase initially and, then, starts to decrease after reaching a maximum value. The VES viscosity was found to have an unusual trend as it showed a maximum viscosity value at a middle range temperature. **Figure 2.3** shows the viscosity behavior of a solution containing 6 vol.% VES and 15 wt.% HCl at different temperatures. Initially, the viscosity increases as the temperature increases from 20 ^{o}C to 70 ^{o}C. Then, the viscosity starts to decrease as the temperature exceeds 70 ^{o}C to 130 ^{o}C (Nasr El-Din et al., 2008). In another study, the same trend was observed for 4 wt.% VES in de-ionized water as shown in **Figure 2.4**. This behavior was noticed to be the same for the different types of surfactants but they show different maximum values. The unusual trend of viscosity behavior as a function of temperature could be attributed to the restriction of the surfactant micelles at different temperatures (Li et al., 2009).

From both Figures, it is shown that the temperature has a significant impact on the VES viscosity. In fact, it is shown that the viscosity of VES doubles with increasing the temperature from normal surface temperatures of 20 to50 ^{o}C in Saudi Arabia to higher common oil reservoir temperatures in Saudi Arabia of 60 to 80 ^{o}C.

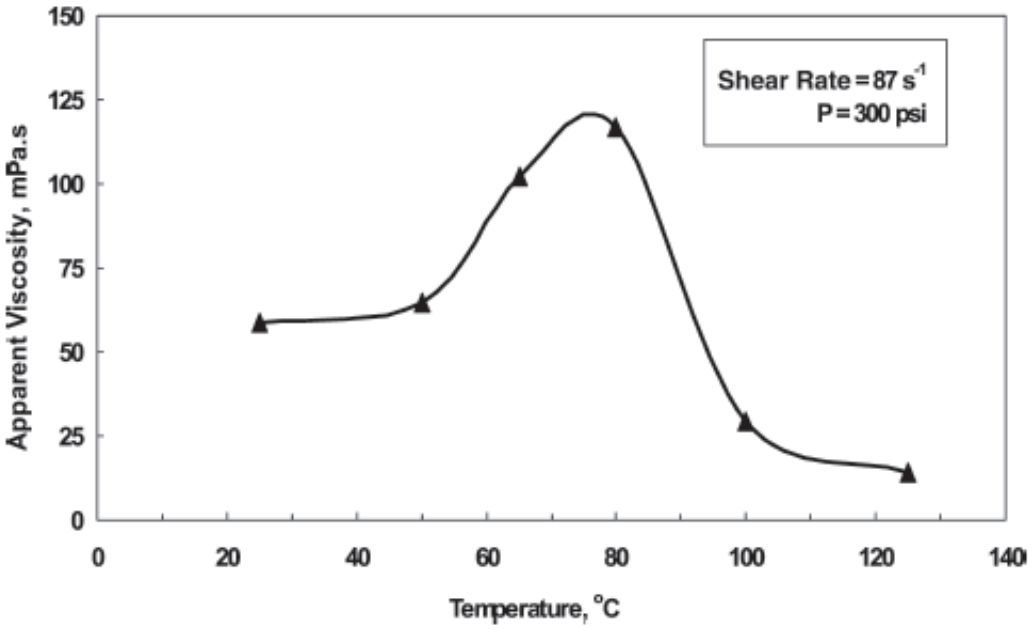

Figure 2.3: Effect of temperature on the apparent viscosity of a live acid containing 6 vol. % of surfactant and 15 wt. % HCl [from Nasr-El-Din et al., 2008]

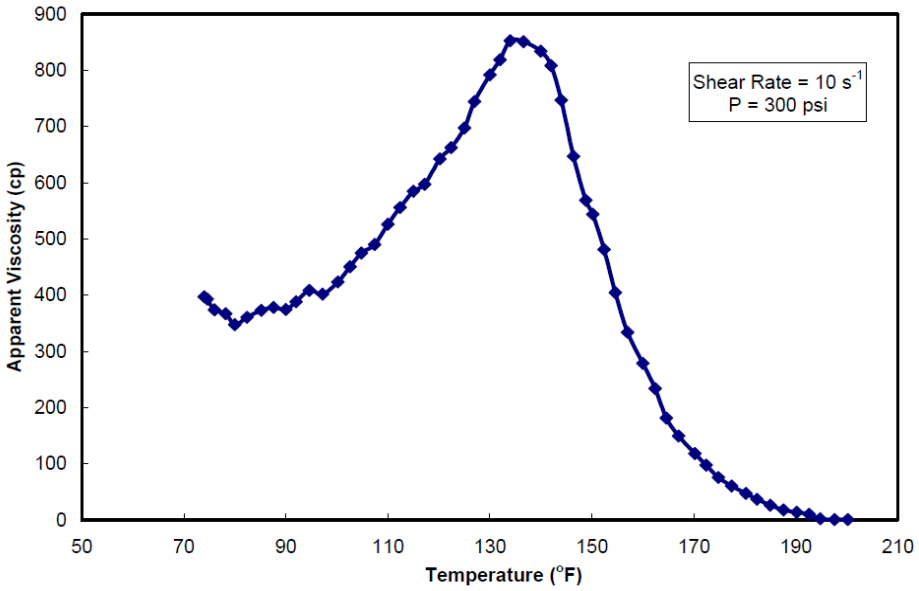

Figure 2.4: Effect of temperature on the apparent viscosity of a 4 wt.% of surfactant solution in de-ionized water [from Li et al., 2009]

The temperature effect was also studied for partially spent 15 wt.% HCl acid VES based system. The partially spent acid was simulated by adding the equavalent amount of generated $CaCl_2$. Different surfactant concentrations were used in the study. The viscosity of each spent acid solution containing different VES concentraion was measured as shwon in **Figure 2.5**. The results show the same trend observed with the live acid VES based systems (Nasr-El-Din et al., 2008).

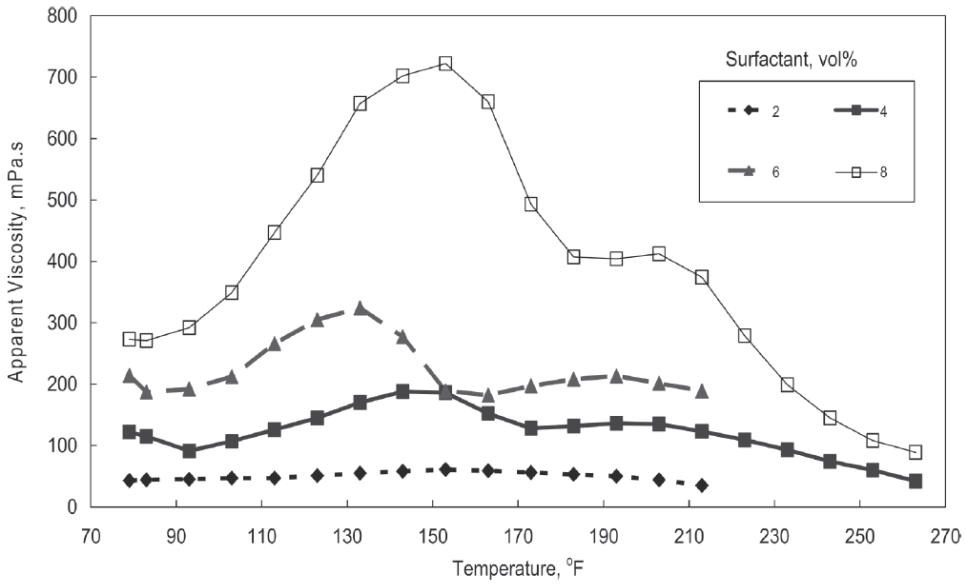

Figure 2.5: Effect of temperature on the apparent viscosity of spent acids containing various concentrations of surfactant [Nasr-El-Din et al., 2008]

2.3.2 Effect of Salinity of Mixing water on VES Viscosity

The effect of the mixing water salinity is important because in field application, salts are added to the live acids to increase the treatment fluid density. The two most common used salts for density increase in the field are NaCl and $CaCl_2$. Recent findings showed that the additions of these salts have an increasing effect on the apparent viscosity of the VES acid system; the higher the concentration of these salts,

the higher is the viscosity of the VES system. **Figure 2.6** shows the effect of adding different calcium chloride concentrations on the viscosity of the VES acid system. From the figure, it is shown that the viscosity is increasing as the concentration of $CaCl_2$ increases in the mixing water. The increase in viscosity is obsereved to be signficant; at 5 VES vol. %, the treatment viscosity increased from 30 to 80 mPa.s as the concentration of $CaCl_2$ increased from 4 to 5 wt.%. Also, it is shown that at different VES concentrations, the impact of the salts concentration is different in magnatiude. The salinity effect gets more significant as the concentration of the surfactant increases (Nasr-El-Din et al., 2007).

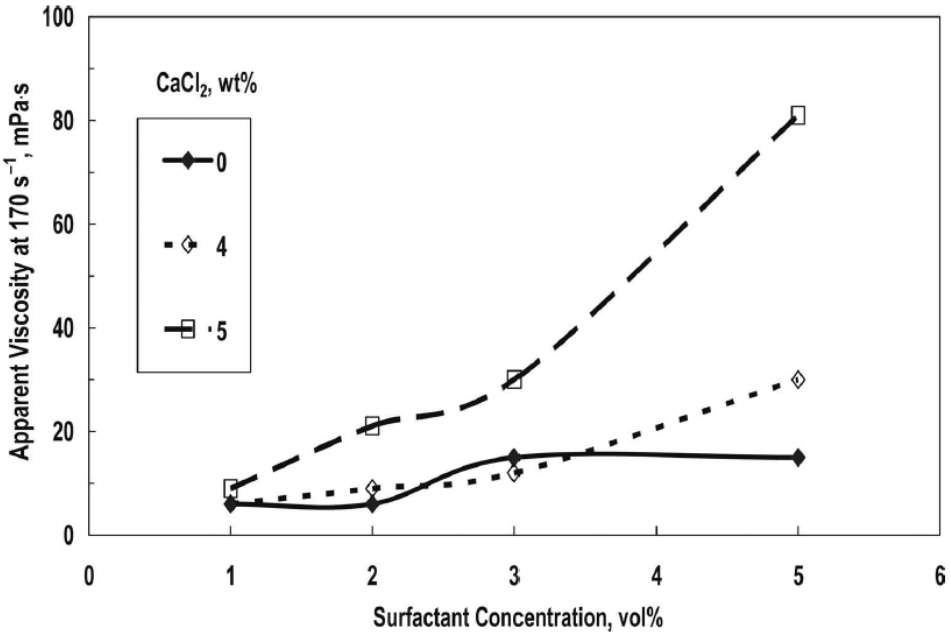

Figure 2.6: Effect of $CaCl_2$ concentration on the apparent viscosity of surfactant solutions at room temperature [Nasr-El-Din et al, 2007]

The addition of the other type of salt, Sodium Chloride, showed the same trend that was observed by adding $CaCl_2$. As shown in **Figure 2.7**, at a surfactant concentration of 5 vol.% without adding NaCl, the viscosity is 15 mPa.s. When NaCl concentration

is increased to 5 wt.%, the viscosity of VES solution increased from 15 to 90 mPa.s. The results observed on increasing the salinity of the carryinf fliud on the VES viscosity is expected due to the VES viscosity build up mechanism which depends heavily on the salts concentration in the fluid (Nasr-El-Din et al., 2007).

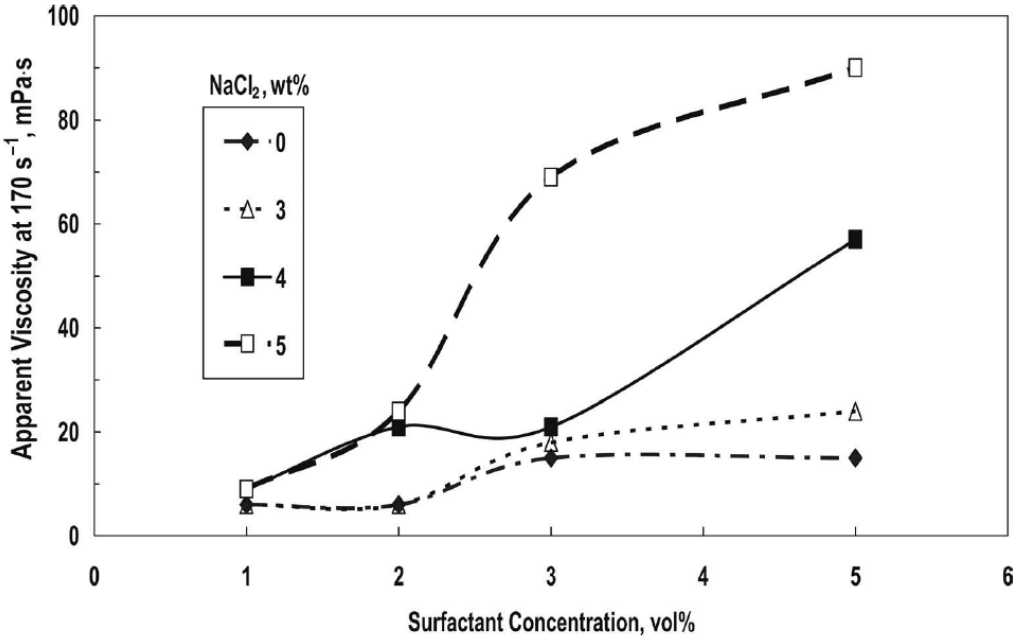

Figure 2.7: Effect of NaCl concentration on the apparent viscosity of surfactant solutions at room temperature [Nasr-El-Din et al, 2007]

2.3.3 Effect of Surfactant Concentration on VES Viscosity

The vescoelastic surfactant concentration effect on the apparent viscousity of VES system is important as it will affect the pumping rates needed to pump the fluid while conducting the stimulation treatment. It was found from a recent study that the VES concentration has a significant effect on the viscousity as shown in **Figure 2.8**. Initially, the viscousity was not increasing significantly but as the cocentration exceeds 3 vol. %, the viscosity starts to have a steep increase. At a concentration of 1

vol %, the viscosity is 12 mPa.s while at 7 vol%, the viscosity increased to 87 mPa.s. A possible explaination of the lower viscosity at low surfactant concentration is the insufficient amount of micelles to entagle and incrase the apparent viscosity of the VES system (Nasr-El-Din et al., 2008).

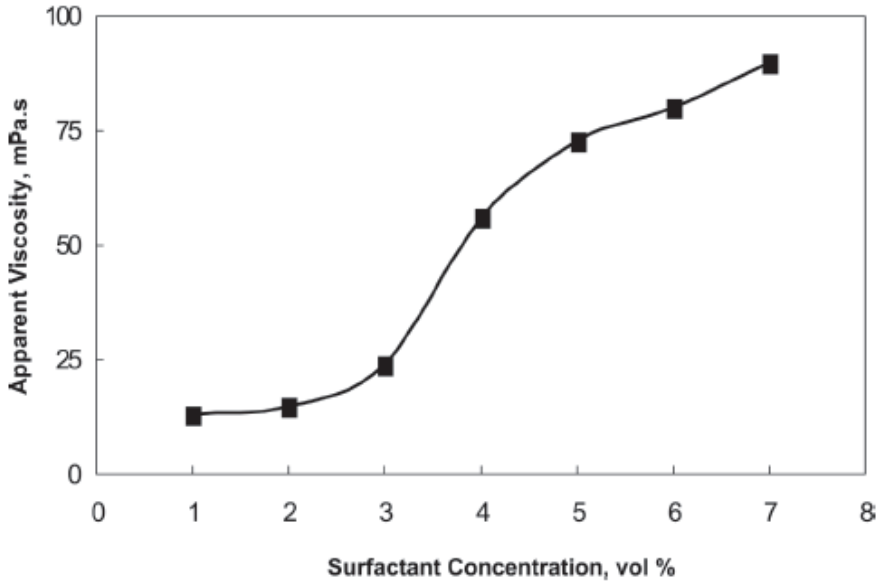

Figure 2.8: Apparent viscosity of live acid containing various surfactant concentrations at 25 ^{o}C [Nasr-El-Din et al., 2008]

The surfactant concentration effect on spent 15 wt.% HCl acid VES-based system was studied. The spent acid was simulated by adding the equavalent amount of generated $CaCl_2$. The viscosity of each spent acid solution containg different VES concentraion was measured and recorded as shwon in **Figure 2.9**. The results show an increasing trend with increasing the surfactant concentration as observed in the live acid VES based system shown in **Figure 2.8** (Nasr-El-Din et al., 2008).

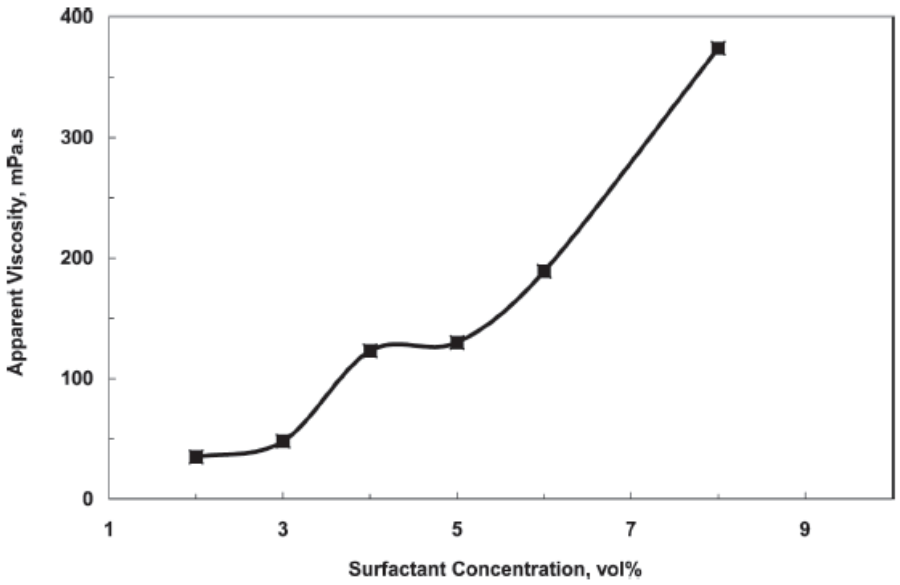

Figure 2.9: Effect of surfactant concentration on the apparent viscosity of spent acid at 100 ^{o}C [Nasr-El-Din et al., 2008]

2.3.4 Effect of Shear Rate on VES Viscosity

The shear rate effect on the viscosity of VES-based acid system is important in the field operations. This is due to the various shear rates that the VES system is subjected to while being transported in the mixing tanks and pumped through the pumps and coiled tubing to the resroiver. The pump rates are usually high and thus, create high shear rate which could damage the surfactant structure in the mixture resulting in a negative impact on visosity. A recent study examied the viscosity of VES system at different shear rates, starting from 58 s^{-1} to 1,740 s^{-1}. The viscosity was measured while increasing the shear rate from 58 s^{-1} to the highest achieved shear rate, 1,740 s^{-1}. Then, the viscosity was measured while reducing the shear rate from 1,740 s^{-1} to 58 s^{-1}. The obtained results show that the high shear rate does not affect the viscosity of VES mixture at low shear rates at a temperature of 25 ^{o}C as shown in **Figure 2.10** (Nasr-El-Din et al., 2008).

The shear rate effect on viscosity is important due to the various shearing rates that the VES system is subjected to while being transported in the mixing tanks and pumped through the pumps and coiled tubing to the resroiver.

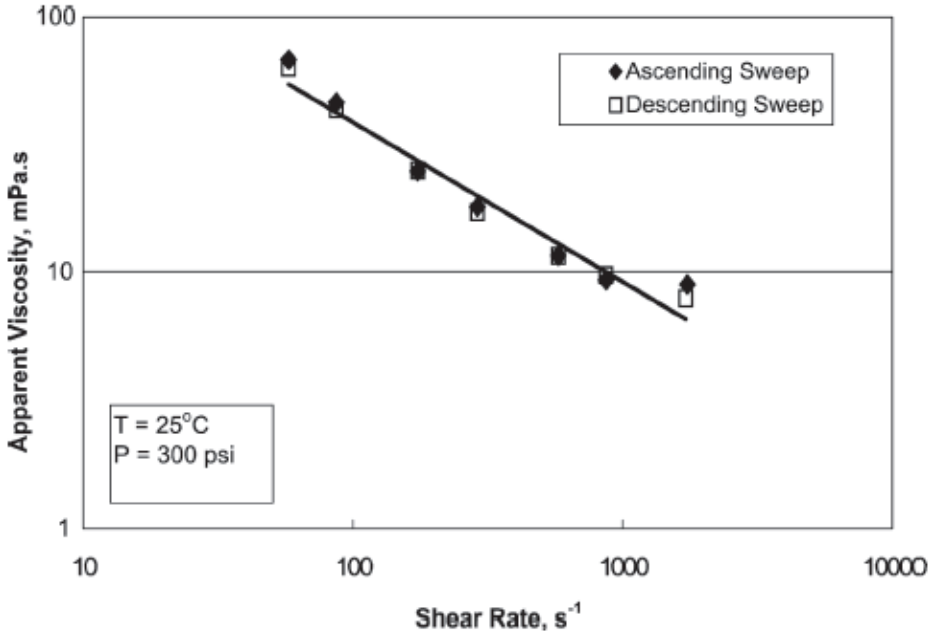

Figure 2.10: Shear-history dependence of the apparent viscosity of a live acid system containing 6 vol.% surfactant at 25 ^{o}C [Nasr-El-Din et al., 2008]

Another set of viscosity measurements at different shear rates was conducted at 100 ^{o}C. When increasing the temperature to 100 ^{o}C and repeating the viscosity measurements of **Figure 2.10**, it showed different behavior. The viscosity behavior of VES was found to be signficiantly affected by the temperature increase to 100 ^{o}C. This was evident by observing different viscosity results when reducing the shear rate back to 58 s^{-1} as shown in **Figure 2.11**. This is possibly because the micelles did not return to the same structure when reducing the shear rate back to the original (Nasr-El-Din et al., 2008).

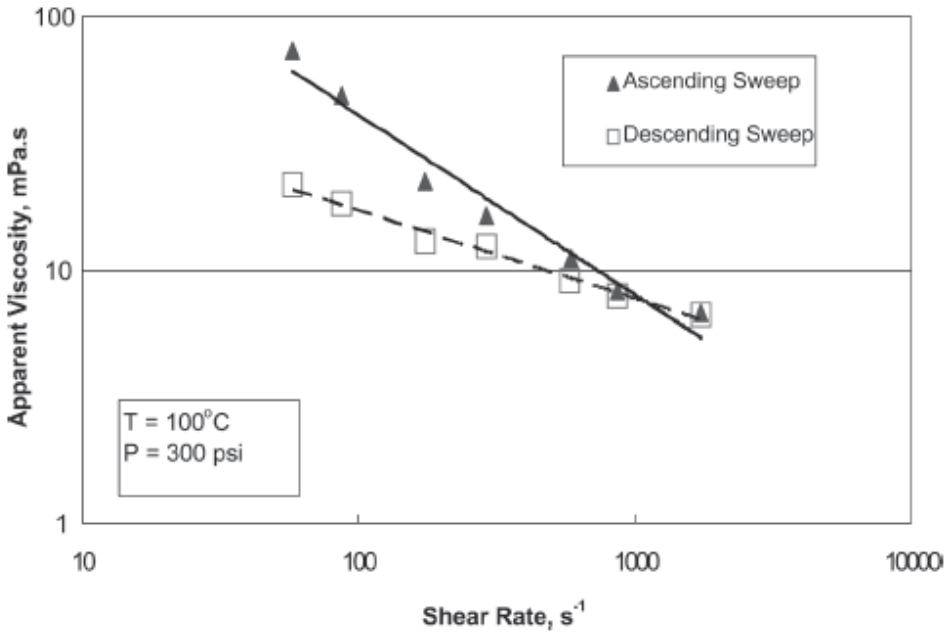

Figure 2.11: Shear-history dependence of the apparent viscosity of a live acid system containing 6 vol.% surfactant at 100 ^{o}C [Nasr-El-Din et al., 2008]

The shear rate effect on viscosity was studied for VES-based spent acids in the same procedure highlighted earlier for VES-based live acids. The tests were conducted at 50 ^{o}C and 100 ^{o}C. Unlike the results generated for live acid VES-based systems, at both temperatgures, spent acids VES based systems showed no significant differece in viscosity values as shown in **Figures 2.12** & **2.13**. This is attirbuted to the effect of calcium ions on stabilizing the rod-like shape of surfactant micelles (Nasr-El-Din et al., 2008).

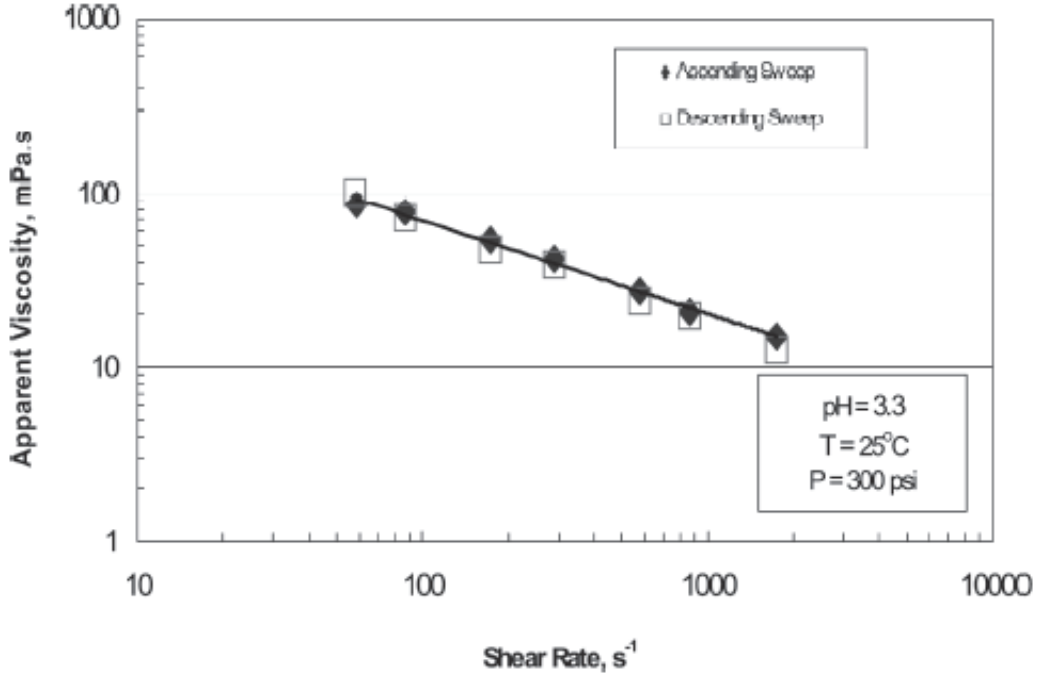

Figure 2.12: Shear-history dependence of the apparent viscosity of a spent acid system containing 6 vol.% surfactant at 25 ^{o}C [Nasr-El-Din et al., 2008]

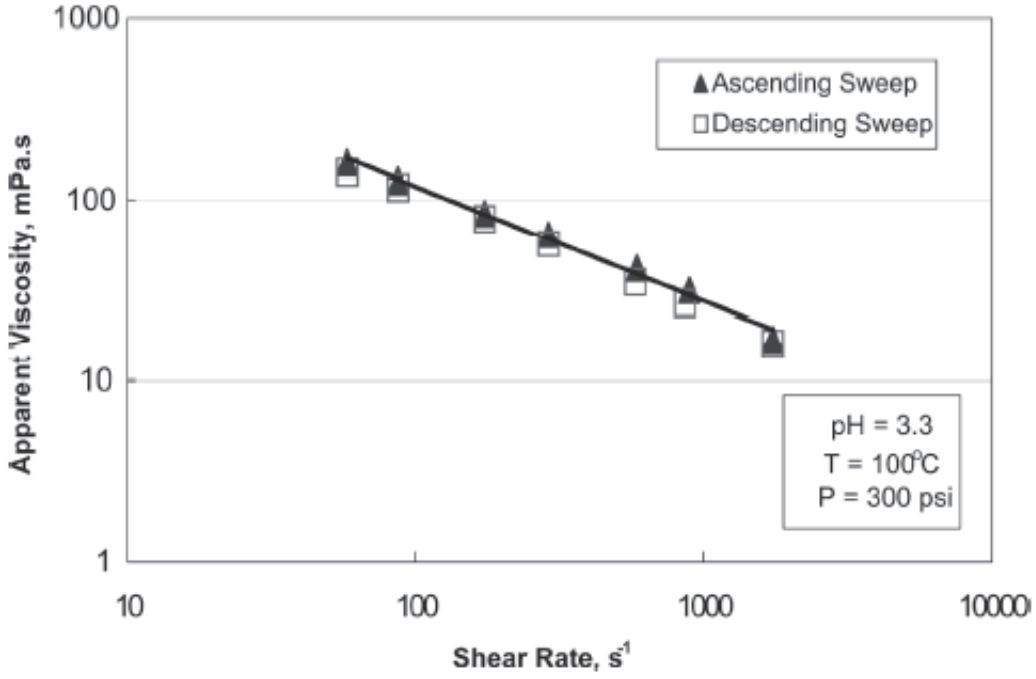

Figure 2.13: Shear-history dependence of the apparent viscosity of a spent acid system containing 6 vol.% surfactant at 100 ^{o}C [Nasr-El-Din et al., 2008]

2.3.5 Effects of Additives on VES Viscosity

VES-based acid systems treatment usually contain different additives that are added for different purposes. For example, additives are added to minimize side reactions and decrease the precipitation tendency of the stimulation treatment. Corrosion inhibitor (CI) is added to inihibt the treatment corrosive effect on the well tubings. The list of different additives are shown in **TABLE 2.1**. A recent study showed the effect of adding two different corrosion inhibitors, CI-A and CI-B, on the viscosity of VES solution. The shear rate applied in the study is 87 s^{-1} and the operating pressure is 300 psi. **Figure 2.14** compares the viscosity of VES system without corrosion inihibitor, with CI-A and with CI-B. As shown in the figure, the addition the corrosion inihibors have different effects as they have different compositions. The effects of other additives are shown in **Figure 2.15** (Nasr-El-Din et al., 2008).

TABLE 2.1: Concentration Range of Acid Additives Examined [Nasr-El-Din et al, 2008]

Additive	Concentration
Corossion inhibitor, A or B	0.6 vol.%
Inhibitor aid (formic acid)	2 and 5 wt.%
Demulsifier	0.5 wt.%
Surfactant (nonionic)	0.5 wt.%
H2S scavenger	0.5 wt.%
Iron control agent (citric acid)	0.5 wt.%
Iron (III)*	5,000 mg/l
Mutual solvent	10 wt.%
Methanol	1 to 10 vol.%
*Ferric chloride was used as a source of Fe (III)	

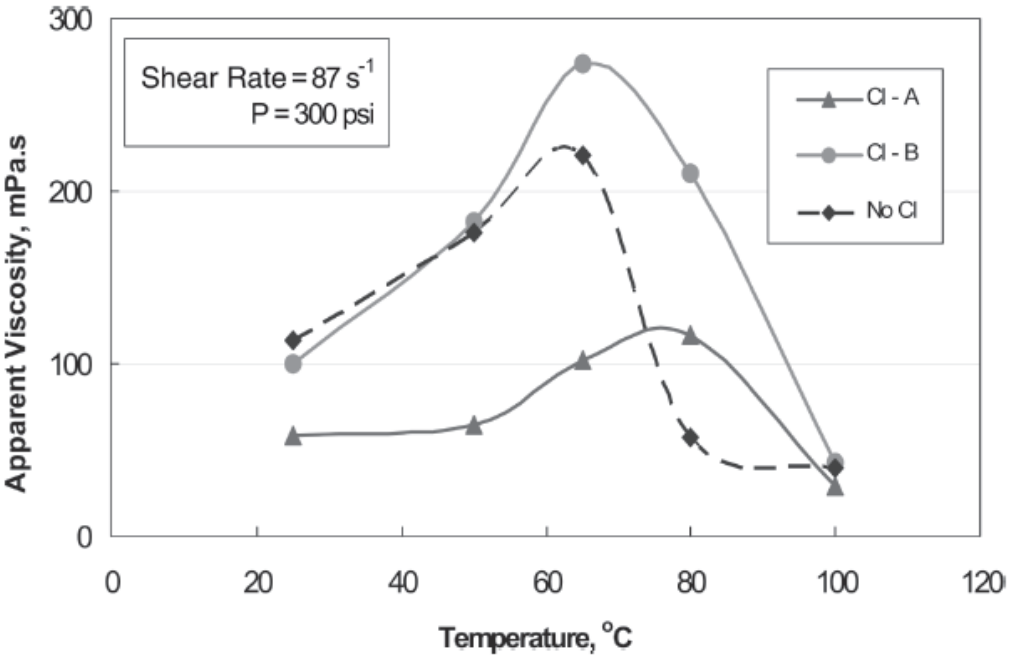

Figure 2.14: Effect of corrosion inhibitors on the apparent viscosity of live acids containing 6 vol.% of surfactant and 15 wt.% HCl [Nasr-El-Din et al, 2008]

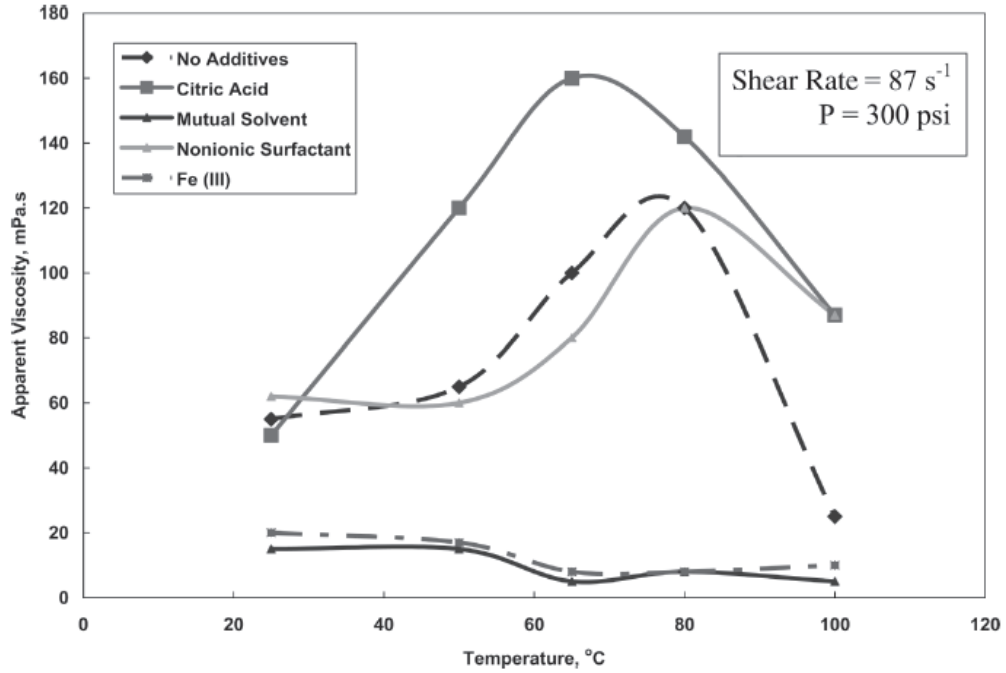

Figure 2.15: Effect of various additives and contaminants on the apparent viscosity of live acid containing 6 vol.% surfactant and 15 wt.% HCl [Nasr-El-Din et al, 2008]

VES-based system viscosity can be reduced significantly by oil or mutual solvent contact with with VES. For oil wells, this can be achieved through flowing back the well. For water injection wells and dry gas wells, mutual solvent has to be injected to break VES-based system viscosity. The effect of mutual solvent on VES viscosity was evaluated and studied using two different concentrations of mutual solvents, 5 wt.% and 10 wt.%. The original solution contains 20 wt.% HCl, 4 wt.% surfactant, and 1 wt.% corrosion inhibitor. The viscosity was measured at different temperatures for three different solutions, one does not contain mutual solvent and the other two solutions cotain 5 and 10 wt.% mutual solvent. The results show that mutual solvent has strong effect in breaking the viscosity of VES and with higher concentration of mutual solvent, further viscosity reduction takes place. At a temperature of 65.6 ^{o}C, the viscosity of the spent acid VES system is around 800 cp but when adding 10% wt. mutual solvent, the viscosity decreased to 1 cp. The results are shown in **Figure 2.16** (Li et al., 2009).

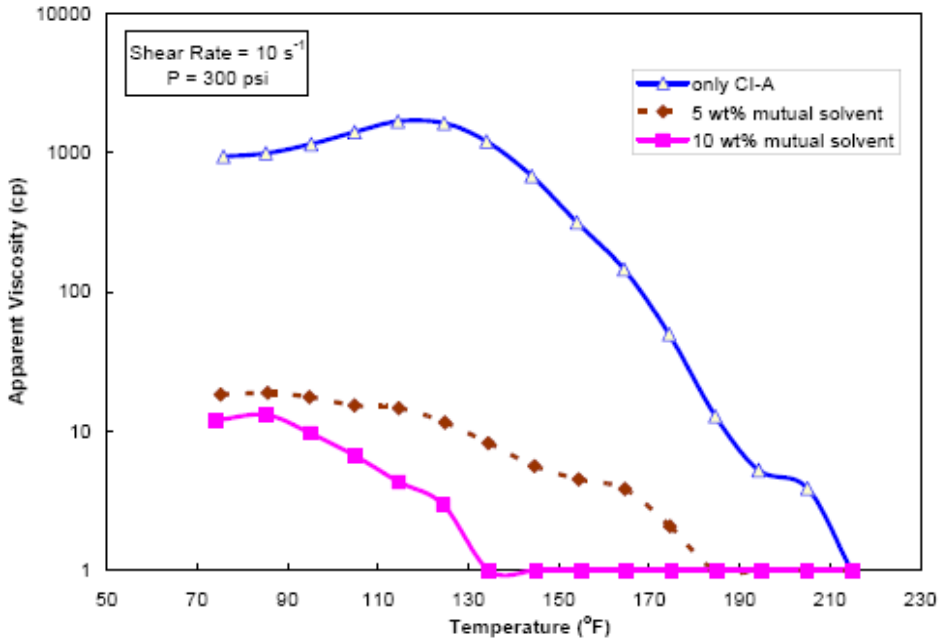

Figure 2.16: Effect of mutual solvent on the apparent viscosity of spent acids (pH = 4-5). All solutions contained CI-A [Li et al, 2009]

2.3.6 Spent acid effect on VES based system viscosity

The viscosity generated due to the effect of spent 28 wt% HCl acid on VES system is a critical value that needs to be determined at different temperatures to have an indication of the viscosity in the formation after full acid reaction. A recent study showed the viscosity increase when 28 wt.% HCl acid is fully reacted. This was studied using three simulation scenarios, full reaction to produce $MgCl_2$, full reaction to produce $CaCl_2$, and mix of both salts. The viscosity was measured at 170 s^{-1} and the equivalent amount of salt was added to represent full reaction of 28 wt.% HCl acid. The surfactant concentration is 5 vol%. As shown in **Figure 2.17**, all spent acid solutions that contain different salts have much higher viscosity than the live 28 wt.% HCl acid. Although $MgCl_2$ salt showed much higher viscosity than the other two mixture solutions at temperature of 75 ^oC, at temperatures above 100 ^oC, the differences in viscosities diminish (Nasr-El-Din et al., 2007).

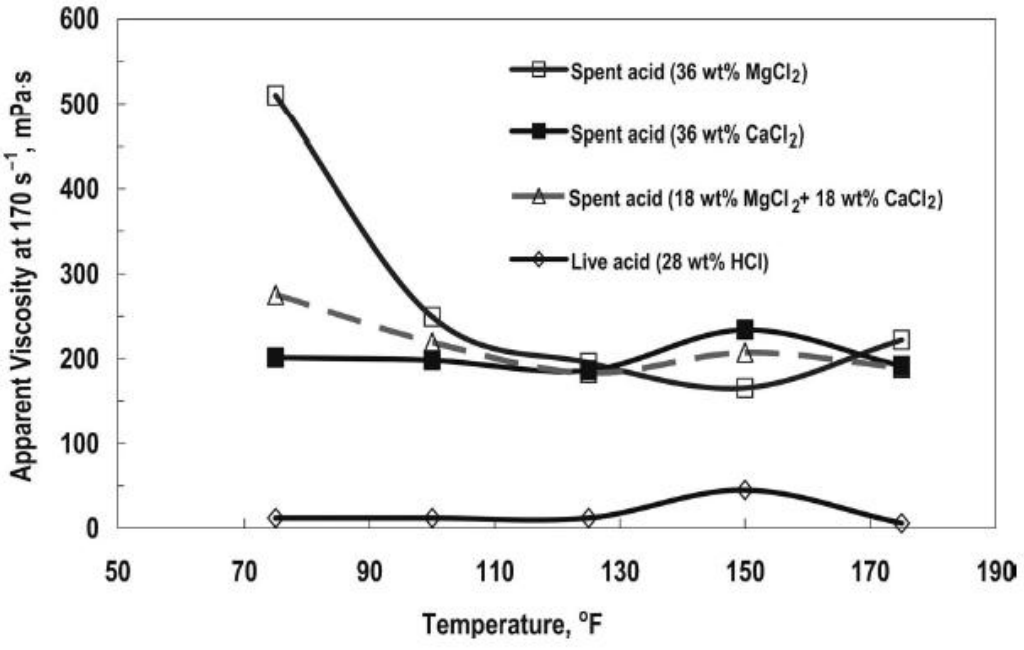

Figure 2.17: Apparent viscosity of 28 wt.% HCl live and spent acids (adjusted to pH of 4) as a function of temperature [Nasr-El-Din et al., 2007]

2.3.7 Effect of pH on the gelation of VES acid system

Acid VES based treatment undergoes different pH values when it is in contact with the reservoir rock. Initially, the pH value is very low and eventually, it increases to 4 as HCl acid reacts with the calcium carbonate and gets spent. The pH value was found to be very critical to the gelation of the VES system even if a large amount of salt is generated and dissolved in the solution. A study was conducted to investigate this effect and it was found that below pH of 1 the gelation is not significant but as the pH value exceeds 2, the solution viscosity increases sharply as shown in **Figure 2.18**. Usually when the VES solution is in the formation, pH will increase above 2 as a result of the acid reaction with the formation carbonate rock. This results in increasing the viscosity of the solution with the presence of the generated salts (Chang et al., 2001).

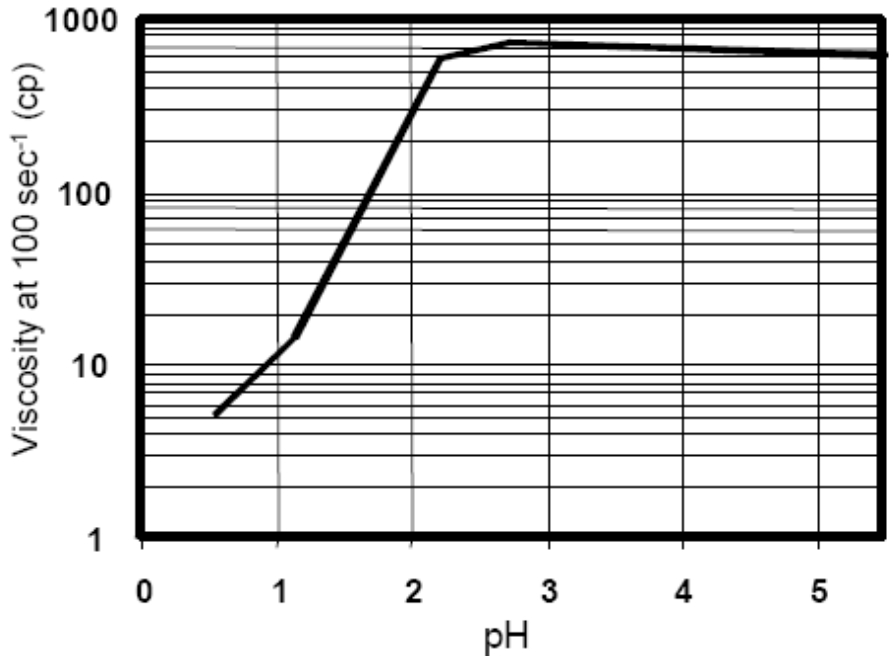

Figure 2.18: Viscosity profile of the VES-based acid as a function of pH at 75 ^{o}F during acid spending [Chang et al., 2001]

2.4 Core flooding Studies

2.4.1 Effect of VES in increasing penetration in carbonate reservoirs

Penetration is an important factor while treating carbonate reservoirs to increase oil productivity. Higher penetration inside the reservoir is always desired to by pass the near wellbore damage and increase productivity or injectivity. Penetration is depicted in the lab by break through time which is the time it takes the treatment to make a channel through the core sample with a pressure drop of almost zero. One of VES system objectives is to increase the penetration rate inside the reservoir. Two experiments were conducted to study the penetration impact of VES when compared to conventional live acid treatment. The two experiments used identical carbonate core samples and were loaded in a core holder with a confining pressure of 2,200 psi, pore pressure of 1,000 psi, and a temperature of 175 ^{o}F (Nasr-El-Din et al., 2007).

The first experiment used 5 wt.% HCl acid system without VES while the second treatment contained 5 vol.% VES in the live acid. Both treatments were injected while automatically recording the pressure drop across the core samples. **Figure 2.19** shows the results for both treatments after injection through the carbonate core samples and reaching the break though time. Due to the viscosity build up effect of VES system, pressure drop of the VES based system kept increasing until the acid system reaches the end of the core sample showing a break through time of 13.5 minutes. The other treatment that doesn't contain VES showed shorter time to break through the core sample of 11 minutes. The VES treatment showed higher pressure drop of 175 psi, whereas it was 127 psi for the regular acid treatment. These results coincide with the VES role in the treatment fluid. While being injected in the carbonate core sample, VES system was generating viscosity as the acid is reacting with the sample to

generate salts. Viscosity generation in the core sample reduced the reaction rate between the HCl acid and the carbonate core sample which delayed the break through time and resulted in more penetration (Nasr-El-Din et al., 2007).

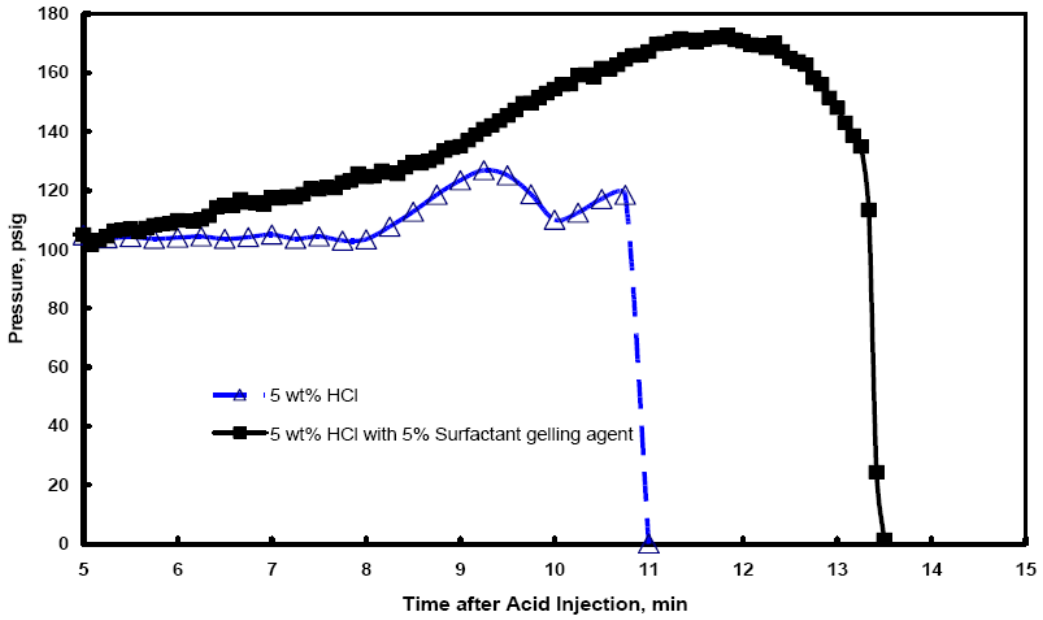

Figure 2.19: Pressure drop across the core during injection of 5 wt.% HCl with and without the surfactant [Nasr-El-Din et al., 2007]

2.4.2 Diversion efficiency of VES acid treatment

The ultimate goal of the VES system is to divert the acid treatment from high permeability zones to lower permeability zones to increase the effectiveness of the stimulation treatment. This role of VES in the stimulation treatment was investigated and studied using core flooding experiments. The samples used in the study are carbonate core samples collected from Indiana limestone cores with a diameter of 1 in. and a length of 4 in. 3% NH_4Cl brine was used to saturate the core samples and establish the base permeability of each sample. The treatment fluid was injected after obtaining the base permeability with a constant injection rate to the three core samples

simultaneously. The VES system treatment contains 15 wt. % HCl. The core flood system apparatus is shown in **Figure 2.20** (Chang et al., 2001).

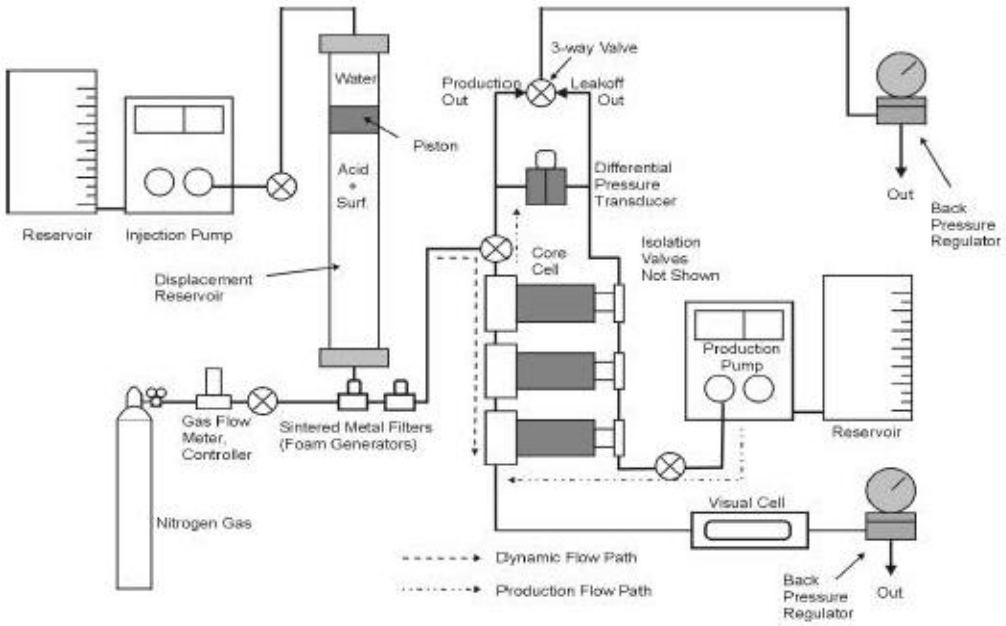

Figure 2.20: Multi-Core flow apparatus for the acid diversion and regained permeability studies [Chang et al., 2001]

They selected core samples to cover the wide range of permeability changes in the reservoir section. The first three samples have permeabilities of 48.7 mD, 35 mD, and 26.8 mD. After VES acid system injection, the permeabilities of the three core samples increased from 48.7 mD to infinite, from 35 mD to 47.2 mD, and from 26.8 mD to 74.8 mD. As shown from the results, the VES system resulted in stimulating both the low and high permeable core samples. Another core flood experiment was conducted using fresh three core samples with permeabilities of 66.5 mD, 34.5 mD, and 32.0 mD. Then, straight 15 wt.% HCl was injected simultaneously in the core samples. The results were significantly different from the results obtained with the VES based treatment. The core sample with permeability 66.5 mD increased to

infinity and the other core samples 34.5 mD and 32.0 mD increased to 34.3 mD and 37.6 mD. As shown from the results, the lower permeability core samples received almost zero enhancements from the acid treatment and the only sample that received significant stimulation is the highest permeable core sample. This shows the benefit gained by adding VES additive where the acid is diverted to lower permeable zones and enhancing the stimulation treatment. **TABLE 2.2** shows the summary of results generated from the core flooding experiments conducted.

TABLE 2.2: Comparison of diversion efficiency and regained permeability for various acid diversion techniques [Chang et al., 2001]

Diversion System	Core	Initial Permeability, (mD)	% Wormhole Penetration	Regained Permeability, (mD)
Straight 15% HCl	1	66.5	100	infinite
	2	34.5	0	34.3
	3	32.0	0	37.6
Polymer based in situ gelled 15% HCl	1	23.1	40	---
	2	112.1	100	infinite
	3	29.6	30	---
Foamed 15% HCl	1	43.7	---	infinite
	2	15.1	---	14.1
	3	37.0	---	31.6
Alternating foam slug and 15% HCl	1	26.1	---	36.1
	2	33.7	---	---
	3	24.9	---	67.5
VES based in situ gelled 15% HCl	1	48.7	100	infinite
	2	35.0	60	47.2
	3	32.1	60	74.8
VES based in situ gelled 15% HCl	1	91.1	100	infinite
	2	39.0	50	54.1
	3	26.8	40	42.3

Another study evaluated the diversion efficiency using higher acid concentration and parallel core flooding equipment. The treatment contains 28 wt. % HCl and 4 Vol.% of VES. The core flooding apparatus is shown in **Figure 2.21**. A confining pressure of 1,500 psi and a back pressure regulator of 500 psi were applied while conducting the experiments. The samples were first saturated with 3 wt.% ammonium chloride and the base permeability was obtained for each sample. Then, the treatment was injected in the injection direction through the two cores simultaneously at a rate of 5 ml/min. Upon reaching a break though, the flow was stopped and the retained permeability was measured. The selected core samples have high permeability contrast. Sample-1 has a permeability of 40 mD while sample-2 has a permeability of 68 mD. After the application of VES acid system, both samples were stimulated and their permeability increased significantly. The permeabilities of sample-1 and sample-2 were increased to 3,000 mD and 2644 mD, respectively. **TABLE 2.3** shows the summary of the parallel core flooding results (Nasr-El-Din et al., 2006).

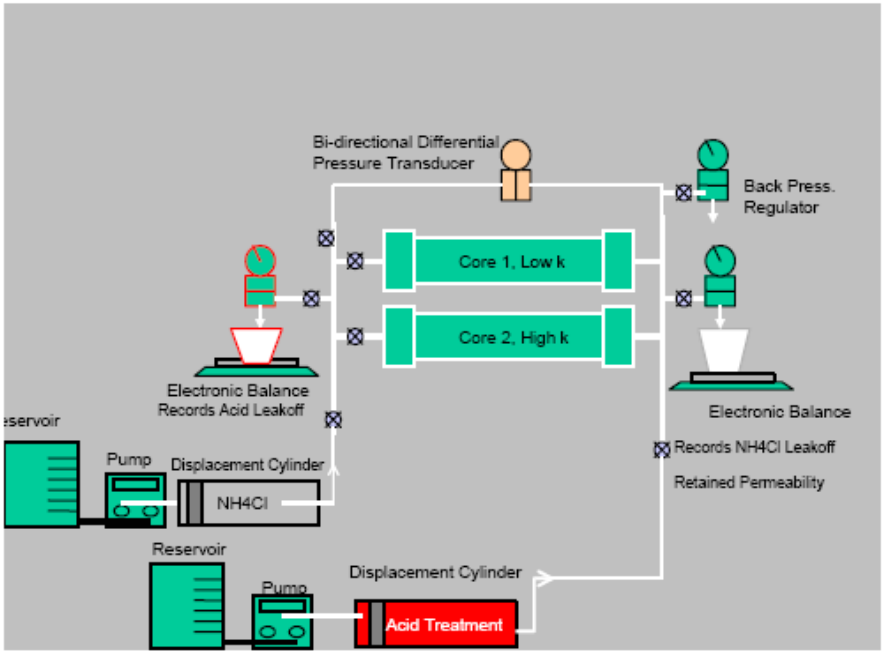

Figure 2.21: Core flood set-up [Nasr-El-Din et al., 2006]

TABLE 2.3: Initial and final permeabilities of two core plugs used in parallel flow testing. The test was performed at 65.6 ^{o}C with 28 wt.% HCl and 4 vol.% surfactant

[Nasr-El-Din et al., 2006]

Core Number	Initial Permeability (mD)	Regained Permeability (mD)
20	38	3,007
24	68	2,644

CHAPTER THREE

MASTER THESIS OBJECTIVES

The purpose of the master thesis was to study the diversion efficiency of VES system, effect of different parameters on the diversion efficiency of VES system and the impact of these parameters its viscosity. For the first time in the industry, the diversion efficiency was studied using 9" long carbonate core samples utilizing return permeability results. The effect of the treatment mixing water salinity was studied over different mixing waters, distilled water, field water, and seawater. Core flooding equipment capable of two parallel core samples was used to study the diversion efficiency of the VES system. The effect of VES concentration on the diversion efficiency of the VES system was evaluated and measured at three values, 1, 3.75, and 7.5 vol.%. In addition, the impact of permeability contrast on the diversion efficiency of VES system was evaluated at various ranges of contrasts using long core samples, 9" long, and 3" in diameter. The temperatures 65.6 and 93.3 ^{o}C were used to evaluate the temperature effect on the diversion efficiency of the VES system. The core flooding experiments were conducted at simulated reservoir conditions of 1,000 psi pore pressure and 2,000 psi confining pressure at 65.6 and 93.3 ^{o}C temperatures.

The viscosity behavior of the VES system was studied over different parameters and in live and spent 15% HCl acid. These parameters include the temperature where it was varied over a long range starting from 21.1 to 121.1 ^{o}C. The mixing water effect on viscosity was evaluated using distilled water, field water, and seawater. The effect of spending 15% HCl on the viscosity of the VES system was measured. Also, the

effect of adding $CaCl_2$ on the VES system viscosity was evaluated. The study covered evaluating of the thermal stability of the VES system in live and spent 15% HCl acid. Different concentrations of VES, 1, 3.75, and 7.5 vol.%, were used to study the effect of VES concentrations on the viscosity. The viscosity results from each parameter were linked to the results generated from the core flooding experiments to offer explanation to the diversion efficiency results.

CHAPTER FOUR

EXPERIMENTAL PROCEDURE

3.1 Materials

The zwitterionic viscoelastic surfactant studied in the master thesis is erucrylamidopropyl betaine supplied by Schlumberger. The product is patented with a patent number 7,119,050 (2006). The VES composition is shown in **Figure 4.1**. The viscoelastic surfactant was supplied as a fresh sample with corrosion inhibitor added to the HCl acid and viscoelastic surfactant to prevent corrosion of the acidic solution while flowing in the core flood lines.

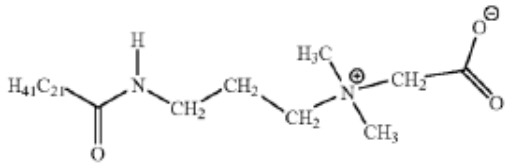

Figure 4.1: composition of VES

To depict the effect of mixing water salinity, three water salinities were used in the study, distilled water, field water and seawater. The distilled water was obtained from the laboratory. The seawater is similar to the Arabian Gulf seawater. The chemical composition and analysis of the seawater used in the study is shown in **TABLE 4.1**. In the experimental work to study the viscosity of VES, different salts were used to study the viscosity change with different salts additions and concentrations.

TABLE 4.1: Field water, distilled water, and seawater chemical analysis [Al-Muntasheri et al., 2007]

Variable	Distilled Water	Field Water	Seawater
Ca	< 1	126	592
Mg	< 1	53	2,304
Na	< 10	228	19,325
K	< 10	14	730
Cl	< 1	361	31,106
SO4	< 1	233	4,108
HCO3	< 1	171	183
TDS	---	1,186	58,348
pH	8.1	7.8	7.9
All Concentrations are in mg/l Total dissolved Solids (TDS) were determined by addition			

The core samples used in the core flooding experiments were collected from Indiana limestone and desert pink limestone outcrops. They have a length of 9" and a diameter of 1.5". A total number of 26 core samples were used in the study experimental study. The chemical compositions of the core samples used are shown in **TABLE 4.2**. Indiana and desert pink limestone cores have the same composition of 100% Calcite. The permeability variations in the samples selected were intentionally chosen to study the permeability contrast effect on the diversion efficiency of the VES

acid system. The core samples used with their permeabilities values in mD are listed in **TABLE 4.3**.

TABLE 4.2: Chemical Composition and Weight Percentage Compounds, Weight Percentage (Wt.%)

	Indiana Limestone	**Desert Pink Limestone**
Calcite [CaCO3]	100	100
Dolomite [CaMg(CO3)2]	0	0

TABLE 4.3: Permeability Ranges of Core Samples used in the Parallel Core Flooding Experiments

Sample Number	Permeability, mD	Sample Number	Permeability, mD
1	0.58	14	2.68
2	0.69	15	4.18
3	0.70	16	4.55
4	0.70	17	4.95
5	0.76	18	6.44
6	0.79	19	27.50
7	0.95	20	30.18
8	0.96	21	31.25
9	0.98	22	34.37
10	1.29	23	37.33
11	1.45	24	40.31
12	2.00	25	40.91
13	2.19	26	56.25

4.2 Preparation

The different solutions and fluids used in the experimental work were prepared using different mixing procedures depending on the additives. The following sections describe the mixing procedure of the experimental fluids.

A. Brines Mixing

The brines used in the study were mixed at different formulations depending on the type of brine prepared. The different brines used in the study were 3% KCl brine, Arabian Gulf seawater, and regular field water shown in **TABLE 4.1**. The brines were mixed first using distilled water and then filtered through 0.3 micron filter paper before using.

B. Acid Mixing

In the study, different acids were prepared at different concentrations and with different additives. Different HCl concentrations are prepared from 37% assay acid container. The acid is mixed after the brine is filtered and prepared. The mixing is conducted using a magnetic stirrer to ensure uniform mixing.

C. VES System Preparation

To prepare the samples, additives were mixed to completely dissolve in the mixing water. Then, the full VES quantity was added to the mixture and mixed for up to 5 minutes using blender. The resultant solution foamed due to the mixing process. The foaming mixture was then degassed through centrifuging for about 5 minutes at 3,000 rpm. The formulation used to prepare VES is shown in **TABLE 4.4**.

TABLE 4.4: 15% HCl acid VES based acid system formulation

Component	Amount
HCl	15 vol.%
VES	7.5 vol.%
Corrosion Inhibitor	0.6 vol.%
Mixing water (D.I., field, or sea water)	76.9 vol.%

4.3 Apparatus

Core flood system

Parallel Core flood equipment was used to study the diversion efficiency of the viscoelastic surfactant based acid system. A schematic diagram of the core flood apparatus is shown in **Figure 4.2**. The core flood system was designed to run two parallel core flooding. The apparatus consists of an oven, positive displacement pumps, accumulators, confining pump, two core holders, back pressure regulator, and data acquisition system.

Each core holder can accommodate a core sample with a diameter of 1.5” and variable length. The core holders were placed inside a temperature-controlled forced-air circulation oven. The positive displacement pumps delivered a consistent and continuous flow rate. Pressure transducers were used to measure pressure drop across the core samples. A back-pressure regulator was used downstream of the core to control flowing pressure. Confining pump was used to keep a constant confining pressure on the core samples during the experiment. Accumulators with floating

pistons were used to store and inject fluids. The data acquisition has the software to control the variables of the experiment such as the fluid flow rate and flow direction. Experimental data was collected using an Excel sheet program installed in the software.

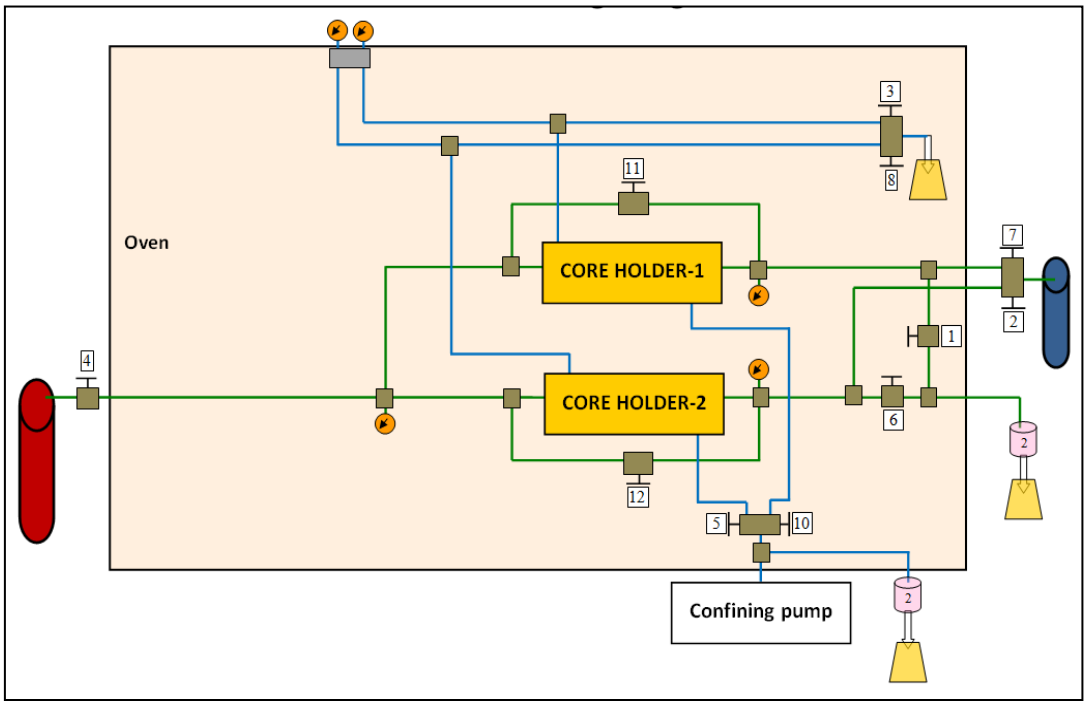

Figure 4.2: schematic of the parallel core flooding apparatus

Viscometer

A rheological stress viscometer was used to conduct the viscosity measurements. The viscometer is shown in **Figure 4.3**. It was used to measure the viscosity of the different solutions prepared in the experimental work at different temperatures. The high pressure cell is sealed and connected to a nitrogen cylinder to allow the pressurization of the sample up to 300 psi and is heated with a controlled heating system.

Figure 4.3: viscometer equipment

4.4 Testing procedure

The following sections describe the main testing procedures followed to generate the results for the thesis experimental work.

4.4.1 Core flooding tests

Base permeability

The core samples are first placed inside the parallel core holders. Then, the confining pump will be used to apply a confining pressure of 2,000 psi to stimulate reservoir confining pressure. The pore pressure was set at 1,000 psi and the temperature of the

oven was set at the desired temperature. After that, 3% KCl brine was injected in the injection direction at a flow rate of 2 mL/min through each mounted core sample until reaching steady state pressure drop across the core samples. This was done in sequence. Once the first sample reaches the steady state base permeability value, the flow is switched to the other core sample for base permeability measurement. The injection direction will be chosen to simulated water injection wells.

The pressure drop across the core sample will be automatically recorded with time. The core samples base permeability values were measured at different flow rates (1, 2, & 4 mL/min). The purpose of the base permeability measurements is to establish a base line for the permeability so that we can measure the enhancement of the treatment on the core samples which will be determined by the retained permeability values.

VES Acid Stimulation System Injection

After establishing the base permeability for the mounted core samples, the treatment is prepared according to **TABLE 4.4** and loaded in the cylinders for injection. The injection of the treatment is in the injection direction to simulate the injection direction of the treatment in the reservoir. The injection rate will be selected to be 5 mL/min. The flow rate will be maintained until one of the core samples encounters breakthrough where the pressure drop goes to almost zero. After that, the pump is directly stopped and the treatment is cleaned from the lines of the system to prepare for establishing the return permeability and measure the enhancement of the treatment on the other core sample.

Return permeability

The return permeability is established by injecting the 3% KCl brine in the injection direction of the core sample at 2 mL/min flow rate until reaching a steady state pressure drop across the core sample. The return permeability values will be used to measure the enhancement of the treatment on the core sample. The permeability of the core sample in the base and return stages will be calculated using Darcy's law as shown in the following section. The enhancement of the treatment will be calculated using Equation-3 as shown below.

Darcy's Law

In calculating the base permeability and return permeability, a linear form of Darcy's law was used. The formula of Darcy's law is as follows:

$$K = \frac{245 \cdot Q \cdot \mu \cdot L}{A \cdot \Delta P} \qquad \text{Equation-3}$$

Where,

K = permeability, md.

Q = fluid flow rate, mL/min.

μ = fluid viscosity, cP.

L = core plug length, cm.

A = core plug cross-section area, cm^2.

ΔP = pressure drop across the core, psi.

Treatment Enhancement (retained permeability)

The retained permeability is defined as the ratio of the return permeability to the base permeability, expressed in percentage. The formula is as follows,

$$K_{rp} = \frac{K_r}{K_b} \times 100 \qquad \text{Equation-2}$$

Where,

K_{rp} = Retained permeability, %.

K_b = Base permeability, md.

K_r = Return permeability, md.

Diversion Efficiency

The diversion efficiency of VES acid system was evaluated by measuring the retained permeability. For each core flood experiment, the obtained retained permeability value was for the tighter core sample as the higher permeability core sample had infinite retained permeability. The retained permeability value was used to compare and rank the diversion efficiencies obtained for different core flood experiments. The higher the retained permeability, the more efficient was the diversion of VES acid system.

4.5 Scope of work and parameters

The master thesis work scope were focused on studying the diversion efficiency of 15% HCl acid VES based system and evaluating several parameters effects on the diversion efficiency. Also, the work investigated the viscosity behavior or live and spent 15% HCl VES based system with different parameters. The following is the list of parameters that were studied and investigated in the master thesis.

- The diversion efficiency of 15% HCl VES based system.
- VES concentration effect on the diversion efficiency of VES system.
- Permeability contrast effect on the VES diversion efficiency.
- Mixing water salinity effect on the diversion efficiency of VES system.
- The temperature effect on the diversion efficiency of the VES system.
- The effect of VES concentration on the viscosity of spent 15% HCl VES based system at different mixing water salinities.
- The effect of $CaCl_2$ on the viscosity of the VES system.
- The effect of the mixing water salinity on the viscosity of spent 15% HCl VES based system.
- The effect of the temperature on the viscosity of the spent and live 15% HCl VES base system at different VES concentrations.
- The effect of spending 15% HCl on the viscosity of the VES system at different temperatures and mixing water salinities.
- The thermal stability of spent and live 15% HCl VES based system.

CHAPTER FIVE

RESULTS AND DISCUSSION

2.1 Experimental Evaluation of Viscoelastic Surfactant Acid Diversion for Carbonate Reservoirs: Parameters and Performance Analysis

2.1.1 Abstract

Formation damage minimization and removal are essential to field productivity enhancement and production target achievement. While formation damage is anticipated during drilling, an effective treatment fluid becomes important to bypass mud damage and enhance well productivity. Most of the fluids used in acid stimulation of carbonate wells are consumed in the high permeable zones - leaving the low permeability and damaged zones not effectively stimulated.

Viscoelastic surfactants (VES) have been introduced in the industry to overcome this challenge and offer effective uniform treatment over long horizontal well intervals to treat damaged and low permeability zones. The viscoelastic surfactant molecules form rod-like micelles in the presence of salt at specific pH condition, which results in significant viscosity increase. Therefore, when added to acid systems, the VES helps in increasing the viscosity of the solution based on the state of the acid-carbonate rock reaction. Customizing the treatment to the field's needs is a key factor to the success of the stimulation treatment. The treatment design includes the mixing water type and VES concentration. These parameters need to be optimized to achieve a uniform distribution of the treatment and effective acid diversion.

This paper studies the diversion ability of VES acid system in comparison to straight acid systems. Also, it evaluates the impact of permeability, salinity, and VES concentration on the diversion efficiency of the VES acid system. For the first time in the industry, the diversion efficiency was shown through return permeability results to be heavily dependent on salinity of the mixing water, VES concentration, and permeability contrast. Increasing the salinity and VES concentration enhanced the diversion efficiency significantly, while increasing the permeability contrast reduced the diversion efficiency.

Core flooding equipment capable of flowing two parallel core samples was used to study the VES acid system diversion efficiency at various permeability contrasts. Carbonate core samples with permeabilities in the range of 0.7-56.25 mD were used in the study. The VES acid system mixing water salinity effect was investigated by comparing the diversion obtained by distilled water, field water and seawater at different VES concentrations. Two VES concentrations were used to evaluate its impact on diversion, 3.75% and 7.5%. These parameters were studied at 1,000 psi for pore pressure, 2,000 psi for confining pressure, and 65.6 ^{o}C for temperature.

5.1.2 Introduction

Matrix acid stimulation treatments are widely applied in the oil and gas industry to enhance the productivity of oil and gas wells and the injectivity of water injection wells. Acid stimulation in carbonate is achieved by creating wormholes inside the reservoir rock. These wormholes increase the reservoir connectivity to the wellbore to allow for higher fluid flow rate. Another objective of acid stimulation is to remove the

near wellbore formation damage caused by drilling and completion fluids (Al-Ghamdi et al., 2009).

Achieving effective stimulation of long horizontal wells with intervals lengths ranging from 3,000 to 5,000 feet is a challenging task. The challenge behind effectively stimulating these wells arises due to mainly the high reactivity of the acid to the carbonate reservoir rock, the drastic permeability contrast, and the length of the targeted interval. If this challenge is not addressed in the treatment program, the acid treatment will flow into the most permeable zones or the least resistance path leaving long intervals of the reservoir section unstimulated.

Diversion of acid stimulation treatments is utilized to address the challenge of stimulating long horizontal wells to achieve effective stimulation and high productivity or injectivity. Acid diversion is classified into two main types, mechanical diversion and chemical diversion. Examples of mechanical diversion include ball sealers. Each of these types has different techniques. Generally, chemical techniques are preferred due to the low cost involved and fewer stages required to achieving effective acid diversion. However, there are other factors that control the selection of the diversion technique such as the well completion type, targeted efficiency, well condition, and economic considerations (Safwat et al., 2002).

As one of the chemical diversion technique, viscoelastic surfactants have been used in the oil industry in the past few years as a diverting additive for acid treatments. This is attributed to their ability to significantly increase the acid viscosity. VES-based acid systems are polymer-free and solids-free systems; this feature makes them almost

non-damaging compared to other chemical diverting techniques (Nasr-El-Din et al., 2004). With the rise of pH value above 2 and the increase in the concentration of the divalent cations (Ca^{2+} and Mg^{2+}) in the spent acid, the viscoelastic surfactants molecules form long worm-like micelles which increase the viscosity of the treatment fluid dramatically. The increase in viscosity is a function of the concentration of the generated salts and the pH of the solution (Chang et al., 2001).

Field results have shown the success of VES when used as a diverting system in acid stimulation treatments. It has shown higher efficiency than other conventional acid-diverter systems. For example, oil production was compared in a field treated with conventional acid treatment and VES based acid treatment. An average of 1,600% more production resulted from wells treated with VES acid systems. In another field data, it was shown that VES divergent technique resulted in a 4 to 5 folds increase in oil production compared to conventional methods. Due to the low volume required in VES-based treatments compared to polymer-based systems, VES is attractive from operational perspective in off-shore environments where tanks and other logistic aspects are critical (Chang et al., 2007).

The purpose of this study is to evaluate the performance of VES acid system used as a divergent system for carbonate reservoirs at 65.6 ^{o}C. The study evaluates the ability of VES acid system in diversion compared to straight acids. Effects of different parameters on the diversion efficiency of VES acid system were investigated. These parameters include the mixing water salinity, permeability contrast, and VES concentration. Parallel core flooding equipment was used to study the diversion

efficiency of the VES acid system. Experiments were conducted at 1,000 psi back pressure, 2,000 psi confining pressure and 65.6 ^{o}C temperature.

Viscoelastic Surfactant (VES)

Viscoelastic surfactants exhibit the ability to align themselves and form wormlike micelles in the presence of salts. This feature results in increasing the viscosity of the VES-based acid significantly. It has been reported that the viscosity is a function of pH; the higher the pH, the more viscous the solution becomes. In general, the viscosity increases dramatically with salt concentration at pH above 2 (Chang et al., 2001).

The viscosity of VES solution develops as a result of the presence of salts such as $CaCl_2$ in the solution and the increase of the pH. This happens when the acid reacts with calcium carbonate rock to produce $CaCl_2$ as shown in Equations 5.1 and 5.2. This scenario takes place when VES acidic system is applied in the wellbore, across the carbonate reservoir rock formation which contains $CaCO_3$ and $CaMg(CO_3)_2$ particles. The products of the acid dissolution reaction increase the solution pH and the concentrations of cations, Ca^{2+} and Mg^{2+}. These two resulting products force the surfactant molecules to align as shown in **Figure 5.1.1** and form rod-like structure (Nasr-El-Din et al., 2008).

$$2\,HCl + CaCO_3 \quad ====> \quad CaCl_2 + CO_2 + H_2O \qquad \text{Equation-5.1}$$

$$2\,HCl + CaMg(CO_3)_2 \quad ====> \quad CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O \qquad \text{Equation-5.2}$$

The resulting shape of the surfactant molecules increases the viscosity of the solution due to the long rod-like structures which entangle and hinder the fluid movement. The

increase in viscosity slows the fluid flow through the higher permeability zones which receives more treatment fluid at the beginning. With more reaction and increase in the viscosity, this zone will be blocked and no more fluid will be allowed to penetrate further. This restriction in fluid movement in the high permeable zones forces the treatment flow to divert to other zones where the permeability is low. (Nasr-El-Din et al., 2008).

Diversion efficiency of VES Acid System

The ultimate goal of the VES acid system is to divert the acid treatment from high permeability zones to lower permeability zones to increase the effectiveness of the stimulation treatment. This role of VES in the stimulation treatment was investigated and studied in several studies. Different parameters were evaluated for their effects on diversion efficiency. The VES acid system as a divergent agent in carbonate matrix acidizing was first developed by Chang et al., (2001). They used triple-core parallel flooding experiments and core samples of 1-inch in diameter by 4-inch in length. The used core samples covered a wide range of permeability contrast to show the benefit gained by adding VES in acid to divert stimulation treatment to lower permeable zones and enhancing the stimulation treatment. **TABLE 1** shows the summary of results generated from their core flooding experiments conducted (Chang et al., 2001). Another study of the diversion efficiency was done by Nasr-El-Din et al., 2006 using higher acid concentration and dual-core parallel core flooding equipment. They used core samples of 1-inch in diameter by 2-inch in length. The treatment contains 28 wt. % HCl and 4 Vol.% of VES. A confining pressure of 1,500 psi and a back pressure regulator of 500 psi were applied while conducting the experiments. The treatment was injected in the injection direction through the two cores simultaneously at a rate

of 5 ml/min. The return permeability results after VES acid injection showed increase in permeability in both core samples indicating diversion ability. **TABLE 5.1.2** shows the summary of their parallel core flooding results (Nasr-El-Din et al., 2006).

5.1.3 Experimental Procedure

5.1.3.1 Materials

Fluids

The viscoelastic surfactant used in this study is a zwitterionic type. The viscoelastic surfactant was used as a fresh sample with corrosion inhibitor added to the HCl acid to prevent the corrosion of the acidic solution while flowing in the core flood lines. To investigate the effect of mixing water salinity, three water salinities were used in the study, distilled water, field water and seawater. The seawater formulation used resembled that of the Arabian Gulf seawater. The field water was a commonly field water used in Saudi Arabia for lab evaluation. The chemical compositions of the seawater and field water used in the study are shown in **TABLE 5.1.3**.

Core samples

The core samples used in the core flooding experiments were collected from Indiana limestone and desert pink limestone outcrops. They have a length of 9” and a diameter of 1.5”. A total number of 26 core samples were used in the study experimental study. The chemical compositions of the core samples used are shown in **TABLE 5.1.4**. Indiana and desert pink limestone cores have the same composition of 100% Calcite. The permeability variations in the samples selected were intentionally

chosen to study the permeability contrast effect on the diversion efficiency of the VES acid system. The core samples used with their permeabilities values in mD are listed in **TABLE 5.1.5**.

5.1.3.2 Preparation

The fluids used in the experimental work were prepared using different mixing procedures depending on the additives. The following sections describe the mixing procedure of the experimental fluids.

Brines Mixing

The brines used in the study were mixed at different formulations depending on the type of brine prepared. The different brines used in the study were 3% KCl brine, Arabian Gulf seawater, and regular field water shown in **TABLE 5.1.3**. The brines were mixed first using distilled water and then filtered through 0.3 micron filter paper before using.

VES acid system Preparation

In the study, 15% HCl concentrations was prepared from 37% assay acid container. The acid was mixed after preparing and filtering the brine. The mixing was conducted using a magnetic stirrer to ensure uniform mixing. Then, the corrosion inhibitor and VES were added using a blender to ensure uniform mixing. The VES was added slowly to the mixture while blending for 5 minutes. The resultant solution foamed due to the mixing process. The foaming mixture was then degassed through centrifuging for 5 minutes at 3,000 RPM. The formulation used to prepare VES is shown in **TABLE 5.1.6**.

5.1.3.3 Apparatus

Parallel Core flood system

Parallel Core flood equipment was used to study the diversion efficiency of the viscoelastic surfactant based acid system. A schematic diagram of the core flood apparatus is shown in **Figure 5.1.2**. The core flood system was designed to run two parallel core flooding. The apparatus consists of an oven, positive displacement pumps, accumulators, confining pump, two core holders, back pressure regulator, and data acquisition system.

Each core holder can accommodate a core sample with a diameter of 1.5" and variable length. The core holders were placed inside a temperature-controlled forced-air circulation oven. The positive displacement pumps delivered a consistent and continuous flow rate. Pressure transducers were used to measure pressure drop across the core samples. A back-pressure regulator was used downstream of the core to control flowing pressure. Confining pump was used to keep a constant confining pressure on the core samples during the experiment. Accumulators with floating pistons were used to store and inject fluids. The data acquisition has the software to control the variables of the experiment such as the fluid flow rate and flow direction. Experimental data was collected using an Excel sheet program installed in the software.

5.1.3.4 Testing procedure

The following sections describe the main testing procedures followed to generate the results for the thesis experimental work.

Base permeability

The core samples were first placed inside the parallel core holders. Then, the confining pump was used to apply a confining pressure of 2,000 psi. The back pressure was set at 1,000 psi and the temperature of the oven was set at 65.6 ^{o}C. After that, 3% KCl brine was injected at a flow rate of 2 mL/min through each mounted core sample until reaching steady state pressure drop across the core samples. This was done in sequence. Once the first sample reaches the steady state base permeability value, the flow was switched to the other core sample for base permeability measurement. The pressure drop across the core sample was automatically recorded with time.

VES Acid Stimulation System Injection

After establishing the base permeability for the mounted core samples, the treatment fluid was prepared according to **TABLE 5.1.6** and loaded in the accumulators for injection. The injection rate was selected to be 5 mL/min. The flow rate was maintained until one of the core samples encountered breakthrough when the pressure drop went to almost zero. After that, the pump was stopped and the treatment was cleaned from the lines of the system. While injecting the treatment, the pressure drop across the samples was automatically recoded with time.

Return permeability

The return permeability was established by injecting the 3% KCl brine at 2 mL/min flow rate until reaching a steady state pressure drop across the core sample. The return permeability values were used to measure the enhancement of the treatment on the core sample. The permeability of the core sample in the base and return stages were calculated using Darcy's law. The enhancement of the treatment was calculated using the following equation.

$$K_{rp} = \frac{K_r}{K_b} \times 100 \quad \text{……..……..} \quad (5.1)$$

Where,

K_{rp} = Retained Permeability, % (Permeability Enhancement)

K_b = Bas Permeability, mD.

K_r = Return Permeability, mD.

Diversion Efficiency

The diversion efficiency of VES acid system was evaluated by measuring the retained permeability. For each core flood experiment, the obtained retained permeability value was for the tighter core sample as the higher permeability core sample had infinite retained permeability. The retained permeability value was used to compare and rank the diversion efficiencies obtained for different core flood experiments. The higher the retained permeability, the more efficient was the diversion of VES acid system.

5.1.4 Results and Discussion

5.1.4.1 Diversion Efficiency of Viscoelastic Surfactant

The viscoelastic surfactant system has been studied in previous work to investigate its diversion efficiency based on return permeability results using carbonate core samples of 2 to 4 inch in length at 65.6 ^{o}C. The first objective of this study was to evaluate the diversion efficiency of the VES acid system using carbonate core samples with higher length. This objective was pursued by conducting parallel core flooding experiments using 9" long carbonate core samples and comparing the obtained results with literature established core flooding results of live-acid systems. Below sections describe the experiments conducted and results obtained.

Diversion Indication by Permeability Enhancement

The first indicator that was used to evaluate the diversion efficiency of the VES acid system was the return permeability resutls obtained from the parallel core flooding experiments. The core flooding experiments were conducted using two carbonate core samples, samples 25 and 11; sample-25 has a base permeability of 40.91 mD where sample-11 has a permeability of 1.45 mD. The permeability contrast between the two samples is 28.2 Folds. The VES acid treatment was injected simultaneously in the two core samples until a breakthrough was reached.

The higher permeablity core sample (sample-25) showed infinite enhancement as a breakthough was reached while injecting the VES acid treatment. The tighter core sample (sample-11) showed an enhancement of 61% in the base permeability of the tighter core sample. This enhancement signifies the diversion efficiency of the VES

acid system as the acid was diverted to the tighter core sample and enhanced its permeability. The results are shown in **Figure 5.1.3**.

As reported in literature, straight acid treatments yield almost no enhancement to the permeability of the tighter core sample. This can be explained as the injected acid will first flow to the higher permeability core sample as it provides the least resistance path for flow. Once the acid reaches the face of the core sample, it will start reacting with the carbonate materials creating more channels and increasing the sample permeability. This will result in stimulating only the higher permeability core sample leaving the tighter core sample unstimulated. This behavior was shown from a recent study (Al-Ghamdi et al., 2010) which examined the permeability enhancement of injecting straight acid in two parallel core samples of 6 mD and 101 mD. Both results generated from this study and the referenced study are shown in **TABLE 5.1.7**.

The results from the VES acid system showed different behavior and results when compared to the straight acid system. The VES acid system is anticipated to favor the higher permeaility core sample at the begining. As more acid reacts with the higher permeability core sample, more viscosity will be generated in the treatment fluid. This will result in hindering the flow and increasing the pressure drop. When the pressure drop reaches a point where it is higher than the pressure drop across the tighter core sample, the VES acid system will be diverted to the other core sample resulting in stimulating both core samples.

VES Acid System Injection Pressure Drop Behavior Compared to Straight Acid System

The pressure drop with time while injecting the VES based acid system was recorded and monitored to evaluate the diversion behavior of the VES acid system. The generated pressure drop was compared with a straight acid injection pressure drop. From literature, the pressure drop obtained from a parallel core flooding experiment is shown to be declining with time in a continues pattern until reaching a breakthough. This can be explained as the acid reacts with the calcium carbonate resulting in creating conductive channels and therefore reducing the pressure drop with time. **Figure 5.1.4** shows a behavior of a pressure drop of a straight acid from a recent study. In the figure, it is shown that the acid results in a continues declines in the pressure drop with time.

Unlike the straight acid system, VES based acid system showed different pressure drop behavior. The pressure drop obtained from the parallel core flooding injection of samples 11 and 25 is shown in **Figure 5.1.5**. As shown in the figure, the pressure drop starts at a value around 33 psi and keeps fluctuating around that value even after 4 minutes of injection. The pressure drop kept fluctuating for more than 50% of the injection time before reaching a breakthrough when pressure drop between the inlet and the outlet of the core sample became almost zero. The fluctuation was followed by a steep increase in the pressure drop by more than 60% of the original pressure drop and then a decline in the pressure drop until reaching a breakthrough at 8.6 minutes. The pressure drop behavior observed while injecting the VES acid system indicates an increase in the fluid viscosity which is believed to be the main reason for the diversion shown in the 61% enhancement in the tight core sample permeability.

Acid Reaction and Fluid Viscosity Counter Effect Behavior

The main reason behind the fluctuation observed in the pressure drop while injecting the VES acid system is attributed to the counter-effect between viscosity change (increase) and the sample permeability increase. The reaction of the HCl acid contained in the VES acid system with carbonate rock results in increasing the permeablity and porosity of the core sample which causes the pressure drop to decrease, meanwhile the fluid viscosity build-up due to produced $CaCl_2$ and increasing pH (above 4) leads to pressure drop increase.

The counter effects of both factors (rock dissolution and fluid viscosity increase) are shown in **Figure 5.1.5**. At the beginning, the effects seem to have equal magnitude resulting in a fluctuating behavior around 33 psi. However, after 4 minutes from injecting VES acid system, the pressure drop increases steeply above 50 psi indicating an overtake by the viscosity effect. Following this stage, a continues decline in pressure drop occurs until reaching a breakthrough indicating a more dominant effect by the dissolution as the effective core length is significantly shortened.

5.1.4.2 Permeability Contrast effect on diversion

Some reservoirs in Saudi Arabia are heterogeneous with high permeability contrasts ranging sometimes from 1 mD to 1,000 mD. Treatments applied on the long horizontal sections of a carbonate reservoir oil well can be exposed to this range. As concluded from the experiments conducted in section-1 of this study, the VES acid system is capable of diverting the acid treatment from high permeable zones to lower permeable zones. However, the diversion efficiency hasn’t been evaluated in previous studies at extreme cases of permeability contrast folds. The objective of this section of

the study is to evaluate the diversion efficiency at wide range of permeability contrasts.

The permeability contrast effect was studied by using carbonate core samples (9" long and 1.5" diameter) with different permeabilities. The core samples were selected from **TABLE 5.1.5** to have various permeability contrasts folds. The studied permeability contrasts used were 3.4, 28.2 and 44.5 folds. The study was evaluated at two VES concentrations, 7.5% VES and 3.75% VES. The sections below describe the results of each.

Permeability Contrast Effect on Diversion Using VES = 7.5%

The first VES concentration that was evaluated is 7.5% VES which is the most commonly used concentration in the field applications. Two core samples were selected (samples 1 and 12) with permeabilities of 0.584 mD and 2.00 mD, respectively, to evaluate the diversion efficiency at the low range of 3.4 folds. The base permeability of the core sample was first established using 3% KCl and followed by VES acid system injection. The results showed that the return permeability of the more permeable sample was infinite while the return permeability of the tighter core sample increased from 0.584 mD to 5.392 mD. The increase in sample-1 permeability corresponded to an enhancement of 824% of its original permeability. The diversion here was shown to be of a high magnitude and this is attributed to the low permeability contrast, 3.4 folds.

The permeability contrast was increased to 28.2 folds using two core samples with permeabilities of 1.45 mD and 40.91 mD. When injecting the VES acid system, the

permeability of the tighter sample increased from 1.45 to 2.33 mD indicating an enhancement of 61%. When compared to the 824% enhancement achieved with 3.4 folds, this result shows that the diversion efficiency decreases with increasing the permeability contrast.

To investigate the limit in permeability contrast at which VES acid system is capable of diverting, a third experiment with higher permeability contrast was conducted, 44.5 folds. The permeability of the core samples was 0.7 mD and 31.25 mD. After injecting the VES acid system, the tighter core sample permeability increased to 0.86 mD indicating a low diversion efficiency of 23%. It is apparent that the VES diverter was not able to divert effectively in such as high permeability contrast. **TABLE 5.1.8** and **Figure 5.1.6** summarize the experiments conducted and results generated. The observed trend of diverting efficiency as a function of permeability contrast could be derived. Although there was diversion in all the three experiments, the permeability contrast showed to be a major factor in diversion efficiency.

The generated diversion enhancements from the three experiments were plotted in **Figure 5.1.7**. The plot shows that the enhancement percentage decreases with increasing permeability contrast. Another observation is that the relationship between the permeability contrast and diversion enhancement is not linear. Increasing the permeability contrast from 28.2 to 44.5 showed much lower impact than increasing the permeability contrast from 3.4 to 28.2 folds. The ratio of enhancement with permeability contrast increase for 3.4 and 28.2 folds is 30.8 while the ratio for 28.2 to 44.5 folds is 2.3. This indicates that the permeability contrast effect on VES acid system diversion would reach a limit, beyond which the VES is no longer to divert,

and that contrast limit could be speculated to be around 60 folds using distilled water. However, when VES is mixed in higher salinity water, the speculated number could be higher as will be shown later in the study.

Permeability Contrast Effect on Diversion Using VES = 3.75%

The permeability contrast effect was evaluated at a lower concentration of VES (3.75% by volume) to evaluate the observed behavior at 7.5% vol. VES. Permeability contrast was selected near to the ones used in the set evaluated at 7.5% VES. The permeability contrasts used are 5.6 and 38 folds. The diversion efficiency was evaluated for each one and compared to each other. For the first permeability contrast, 5.6, two core samples (samples 17 and 19) were selected with permeabilities of 4.95 mD and 27.50 mD, respectively.

After injecting VES acid system, the permeability increased to 6.54 mD indicating an enhancement of 32%. When increasing the permeability contrast to 32 using two core samples (samples 9 and 23) with permeabilities of 0.98 mD and 37.33 mD, respectively, the enhancement achieved decreased to 8% in the tight core sample. The results of the experiments are shown in **Figure 5.1.8**. Diversion was achieved in both contrasts but they showed different enhancements. VES acid system at concentration of 3.75% showed a decrease in diversion efficiency when increasing the permeability contrast.

5.1.4.3 VES Concentration effect on Diversion

The concentration of the viscoelastic surfactant is believed to have a direct impact on the diversion efficiency of the VES acid system as the VES component is the

responsible material for diversion. To evaluate the effect of VES concentration on diversion, the concentration was reduced by 50% (7.5% to 3.75%) and the results were compared to the ones obtained with 7.5% VES. The effect of VES concentration was depicted by running several parallel core flooding experiments using different permeability contrasts. The two contrasts that were used are 38 and 44.5. The higher folds, 44.5, were used with the system containing 7.5% VES while 38 folds were used with the system containing 3.75% VES. In this study, it was not feasible to compare exactly the same permeability contrast due to the diversity in the core samples permeabilities.

Using 3.75% VES and core samples with 38 folds permeability contrast yielded a diversion efficiency of 8% whereas using 7.5% VES and core samples with 44.5 folds resulted in 23% enhancement. The permeability contrast was lowered for the experiment that used 3.75% VES which should allow for more diversion as found in section-2. However, due to the reduction in the VES concentration, the diversion efficiency decreased dramatically. As shown clearly by the results, the decrease in VES concentration from 7.5% to 3.75% causes a dramatic decrease in the diversion efficiency. The results are shown in **Figure 5.1.9**.

Similar observation on the effect of VES concentration was made by comparing the diversion efficiency of using 3.75% VES in permeability contrast of 5.6 versus using 7.5% VES in permeability contrast of 28.2. The results shown in **Figure 5.1.10** indicate that the 3.75% VES resulted in 32% enhancement in 5.6 fold permeability contrast core samples whereas the 7.5% VES achieved 61% diversion efficiency in the 28.2 fold permeability contrast core samples.

The generated results from the conducted experiments indicate that the diversion efficiency is a strong function of VES concentration. This can be explained as the diversion achieved with the VES acid system is a result of the viscosity generated by the VES interaction with the HCl acid reaction products. Increasing the VES concentration will increase the VES molecules present in the solution which will offer more viscosity to the reacted solution. The higher viscosity fluid will increase the blocking effect of the VES acid system resulting in more diversion.

5.1.4.4 Salinity Effect on Diversion

The salinity of the mixing water usually varies based on the available water or salts and the required mixing water density. In this section of the study, the effect of the mixing water salinity on the diversion efficiency of the viscoelastic surfactant system was studied. The study covered two extreme salinity ranges and a middle salinity. These are seawater (high salinity), field water (mid salinity), and distilled water (low salinity). The salinity effect of the mixing water was evaluated at two concentrations of VES, 3.75% and 7.5%. Properties and composition of the water samples are shown in **TABLE 5.1.3**.

The three different salinity water samples were used to prepare HCl and then mixed with the other components in the VES acid system. Each solution was used to stimulate two core samples in parallel core flooding experiment and the diversion efficiency was measured for each. Although some experiments have different permeability contrast, they were chosen to be higher with increasing salinity to depict the diversion impact.

Salinity Effect on VES Diversion Using VES = 3.75%

The salinity impact was first evaluated at VES concentration of 3.75% using seawater and field water. For the seawater and field water salinities, core samples with permeability contrast of 31 folds were used to measure the diversion efficiency. As shown in **Figure 5.1.11**, using seawater as the mixing water, the obtained diversion efficiency was 73%. When using the field water as a mixing water, the diversion efficiency was reduced to 61%. The reduction in the diversion efficiency shows the effect of salinity on the diversion efficiency of VES acid system. These results indicate that increasing the salinity from field water to seawater results in more diversion.

The observation obtained from comparing the diversion of seawater and field water was further investigated by using lower salinity water, distilled water. Two permeability contrasts of 38 and 80.5 were used to evaluate the diversion of VES acid system using the mixing waters, distilled water and seawater, respectively. The VES acid system with distilled water as mixing water resulted in a diversion efficiency of 8% using 38 fold permeability contrast core samples. Using the seawater as mixing water for the VES acid system, the diversion efficiency came out to be 18% using the 80.5 folds core samples. Although the permeability contrast (80.5 folds) in the seawater mixing water was much higher than the permeability contrast (38 folds) in the distilled water mixing water, it gave 10% higher in permeability enhancement. The results are shown in **Figure 5.1.12**.

These results indicate that the salinity of the mixing water of the VES acid system has a significant impact on the diversion efficiency of the system. The results show that

the diversion efficiency is proportional to the salinity of the mixing water within the salinity range in this study. The higher the salinity, the higher is the diversion efficiency of the VES acid system. In the field, this is more desirable as it is easier to obtain saline water than low salinity water in most areas. The high salinity was shown to help in achieving a diversion even if the treatment is applied in a very high contrast permeability carbonate reservoir.

Salinity Effect on VES Diversion Using VES = 7.5%

The concentration of VES was increased to 7.5% and the salinity effect on VES diversion was evaluated. The water types used to evaluate the salinity at 7.5% VES are field water and distilled water using permeability contrasts of 50.2 and 44.5, respectively. The stimulation of the 44.5 folds core samples using the distilled water as a mixing water resulted in an enhancement in the tighter core of 23%. When increasing permeability contrast to 50.2 and using field water mixed VES acid system, the enhancement increased to 35%. **Figure 5.1.13** shows the diversion effect results of the salinity change. Although the 44.5 folds core sample was more favorable to get more diversion as shown in section-2, the higher salinity in the field water was able to overcome the contrast difference and enhance the diversion of VES acid system. The results generated at 7.5% VES confirms the trend observed at 3.75% VES; increasing the salinity resulted in increasing the diversion efficiency.

The salinity effect in enhancing the diversion efficiency of the VES acid system is attributed to the viscosity impact of having higher salinity mixing water. The increased VES fluid viscosity in the higher salinity water is believed to be due to the

interaction of the VES materials of the treatment with the mixing water salt ions such as $CaCl_2$. In the seawater, the concentration of Ca^{++} is 592 mg/L where in the field water, it is 126 mg/L. For the Cl^-, its concentration in the seawater is 31,106 mg/L whereas in the field water, it is 361 mg/L. For the distilled water, the concentration of both ions is very low. There are other ions as shown in **TABLE 5.1.3** which could have an impact as well on viscosity. The significant differences in salts ion concentrations in the three types of waters used in the study are believed to be the reasons behind the obtaining different diversion results.

The salinity effect in 3.75% VES was shown to have more impact by increasing the salinity from zero to field water than increasing the salinity from field water to seawater. Although there is a proportional relationship between the salinity and the diversion efficiency, there seem to be a decreasing effect of the salinity on diversion efficiency. Comparing the distilled water and field water to seawater, there is a diversion enhancement increase with a decreasing magnitude which suggests that there might be a plateau value where salinity doesn't have any more effect on increasing diversion.

5.1.5 Conclusions

Diversion efficiency of VES-based acid was investigated and the effects of various parameters on diversion were evaluated. The following conclusions can be drawn:

1. VES acid system has a significant impact on diverting HCl acid from higher permeability core samples to lower permeability cores samples.

2. The VES acid system showed a diverting effect on HCl at high permeability contrasts of 80.5 folds.
3. The VES acid system diversion efficiency was found to have an inverse relationship with the permeability contrast; the higher is the permeability contrast; the lower is the diversion efficiency of VES acid system.
4. The concentration of VES showed a strong effect on the diversion efficiency; lowering the VES concentration resulted in lowering the diversion efficiency of the VES acid system.
5. The salinity of the VES treatment mixing water was found to be of a significant impact on the diversion efficiency of the VES acid system; higher mixing waters salinity yielded higher diversion efficiency.

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TABLE 5.1.1: Comparison of diversion efficiency of various acid diversion techniques [Chang et al., 2001]

Diversion System	Core	Initial Permeability, (mD)	% Wormhole Penetration	Regained Permeability, (mD)
Straight 15% HCl	1	66.5	100	infinite
	2	34.5	0	34.3
	3	32.0	0	37.6
Polymer based in situ gelled 15% HCl	1	23.1	40	---
	2	112.1	100	infinite
	3	29.6	30	---
Foamed 15% HCl	1	43.7	---	infinite
	2	15.1	---	14.1
	3	37.0	---	31.6
Alternating foam slug and 15% HCl	1	26.1	---	36.1
	2	33.7	---	---
	3	24.9	---	67.5
VES based in situ gelled 15% HCl	1	48.7	100	infinite
	2	35.0	60	47.2
	3	32.1	60	74.8
VES based in situ gelled 15% HCl	1	91.1	100	infinite
	2	39.0	50	54.1
	3	26.8	40	42.3

TABLE 5.1.2: Initial and final permeabilities of two core plugs used in parallel flow testing. The test was performed at 65.6 ^{o}C with 28 wt.% HCl and 4 vol.% surfactant [Nasr-El-Din et al., 2006]

Core Number	Initial Permeability (mD)	Regained Permeability (mD)
20	38	3,007
24	68	2,644

TABLE 5.1.3: Field water and seawater chemical analysis [Al-Muntasheri et al., 2007]

Variable	Field Water	Seawater
Ca	126	592
Mg	53	2,304
Na	228	19,325
K	14	730
Cl	361	31,106
SO4	233	4,108
HCO3	171	183
TDS	1,186	58,348
pH	7.8	7.9
All Concentrations are in mg/l Total dissolved Solids (TDS) were determined by addition		

TABLE 5.1.4: Chemical Composition and Weight Percentage Compounds, Weight Percentage (Wt.%)

	Indiana Limestone	**Desert Pink Limestone**
Calcite [CaCO3]	100	100
Dolomite [CaMg(CO3)2]	0	0

TABLE 5.1.5: Permeability Ranges of Core Samples used in the Parallel Core Flooding Experiments.

Sample Number	**Permeability, mD**	**Sample Number**	**Permeability, mD**
1	0.58	14	2.68
2	0.69	15	4.18
3	0.70	16	4.55
4	0.70	17	4.95
5	0.76	18	6.44
6	0.79	19	27.50
7	0.95	20	30.18
8	0.96	21	31.25
9	0.98	22	34.37
10	1.29	23	37.33
11	1.45	24	40.31
12	2.00	25	40.91
13	2.19	26	56.25

TABLE 5.1.6: VES based acid system formulation.

Component	**Amount**
HCl	15 vol.%
VES	7.5 vol.%
Corrosion Inhibitor	0.6 vol.%
Mixing water (D.W., field, or seawater)	76.9 vol.%

TABLE 5.1.7: Straight acid and VES based Acid systems Enhancement results.

	Regular 15% HCL Acid **[Al-Ghamdi et. Al. 2010]**	**VES-Based 15% HCl Acid**
Core Sample-1 Permeability, mD	101	40.9
Core Sample-2 Permeability, mD	6	1.45
Contrast, Folds	16.8	28.2
Enhancement in Core Sample-1, %	Infinite	Infinite
Enhancement in Core Sample-2, %	0	61

TABLE 5.1.8: Core flooding results of evaluating the diversion efficiency of VES acid system using different core folds.

Experiment Number	Core Sample #	Initial Permeability, (mD)	Permeability Contrasts, Folds	Enhancement, %
1	1	0.58 mD	3.4 Folds	824 %
	12	2.00 mD		Infinity
2	11	1.45 mD	28.2 Folds	61 %
	25	40.91 mD		Infinity
3	4	0.7 mD	44.5 Folds	23 %
	21	31.25 mD		Infinity

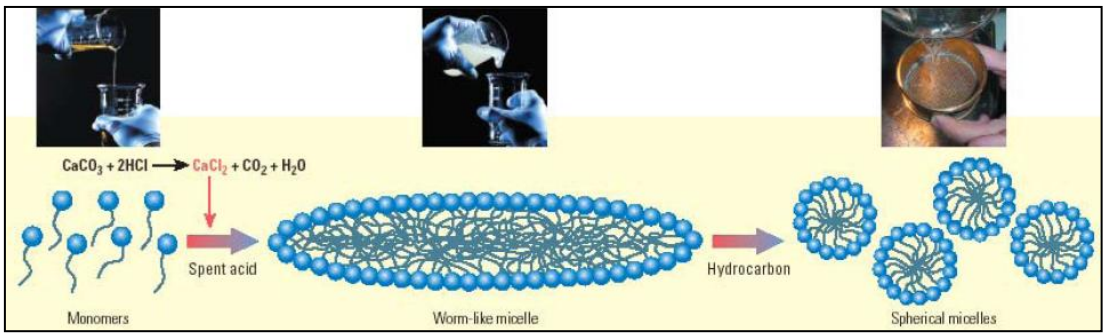

Figure 5.1.1: Illustration of VES structural changes due to acid spending and reaction with hydrocarbons [Nasr-El-Din et al., 2008]

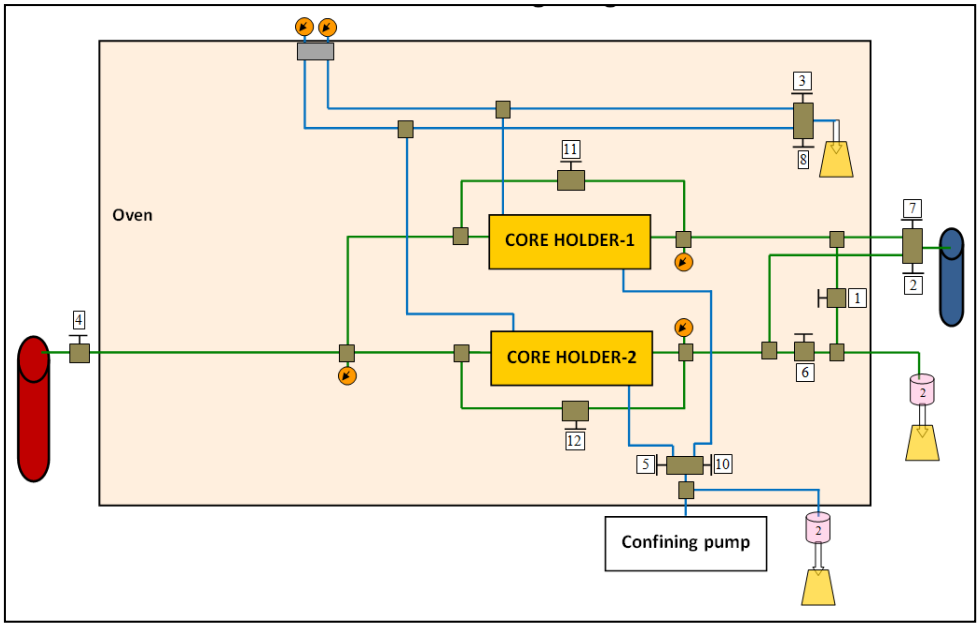

Figure 5.1.2: Schematic of the parallel core flooding apparatus

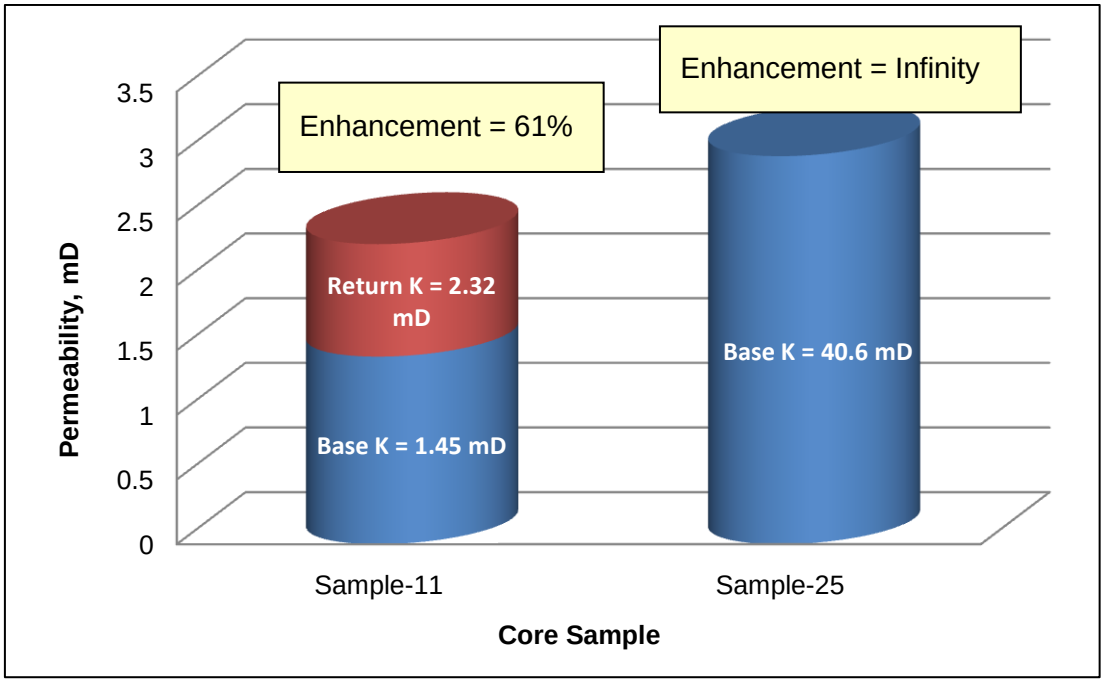

Figure 5.1.3: The diversion efficiency of the VES based acid system using carboante core samples with permeability contrast of 28.2 folds.

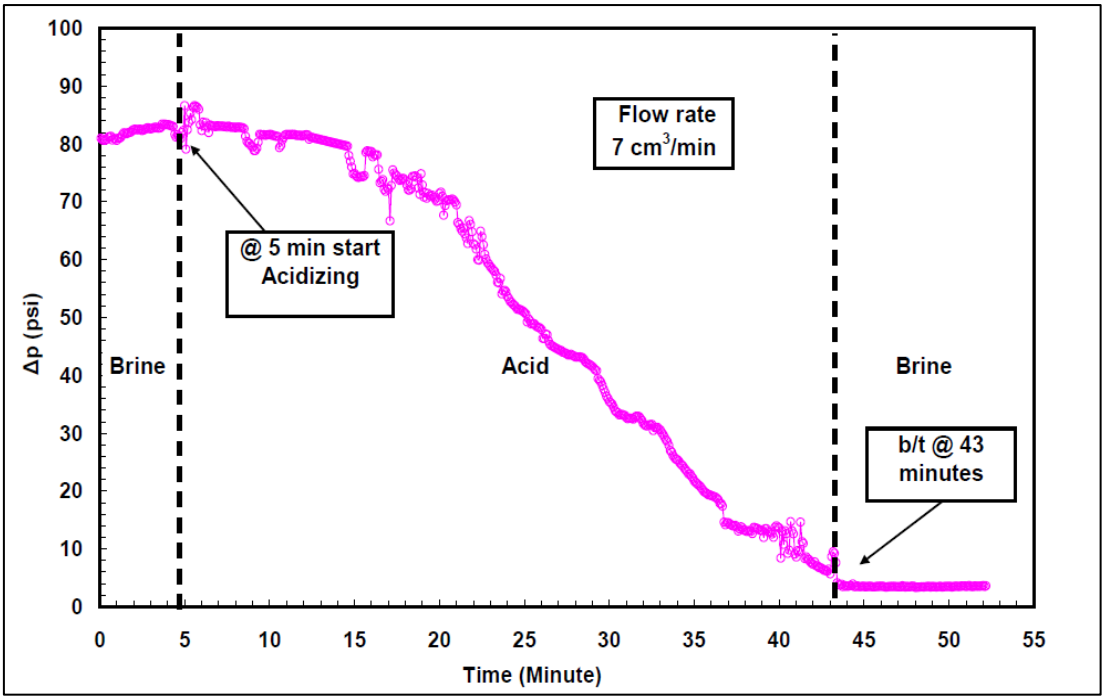

Figure 5.1.4: Pressure drop across the parallel core: regular Acid [Al-Ghamdi et. Al. 2010]

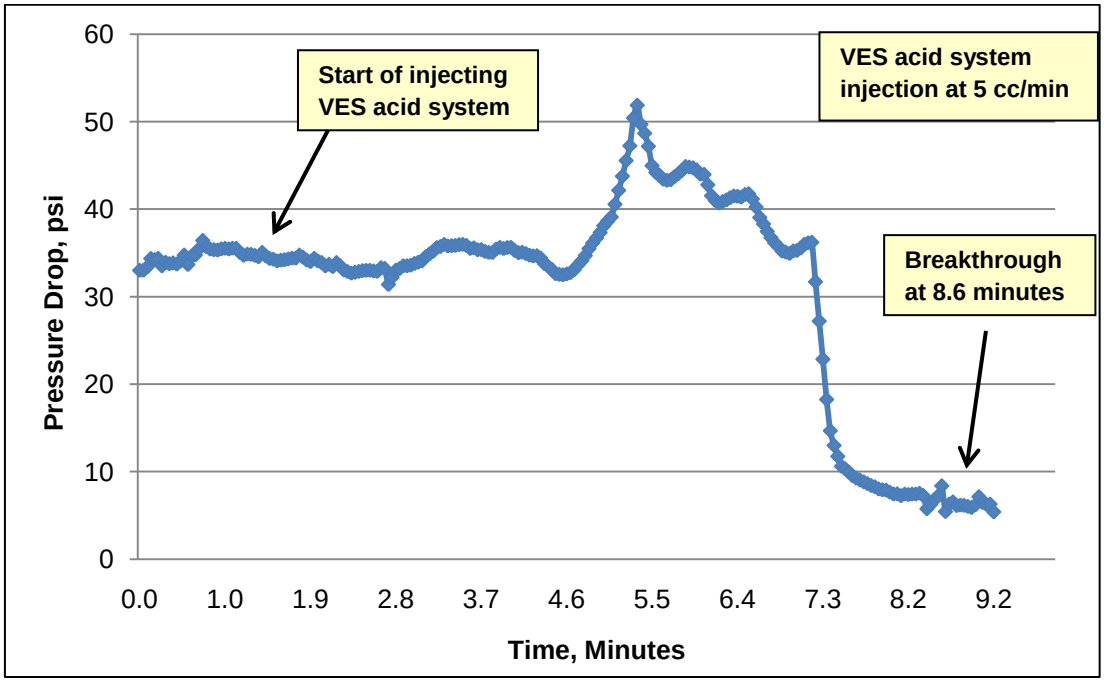

Figure 5.1.5: Pressure drop across the parallel core: VES based Acid System

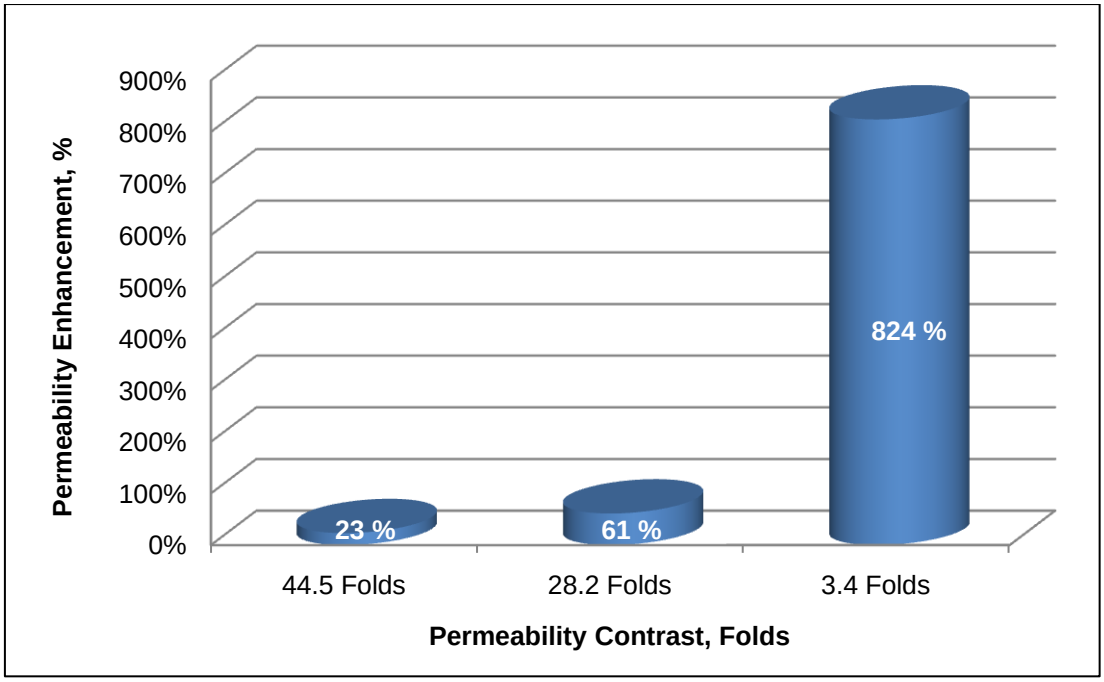

Figure 5.1.6: Permeability Contrast Effect on Diversion Efficiency of VES acid system.

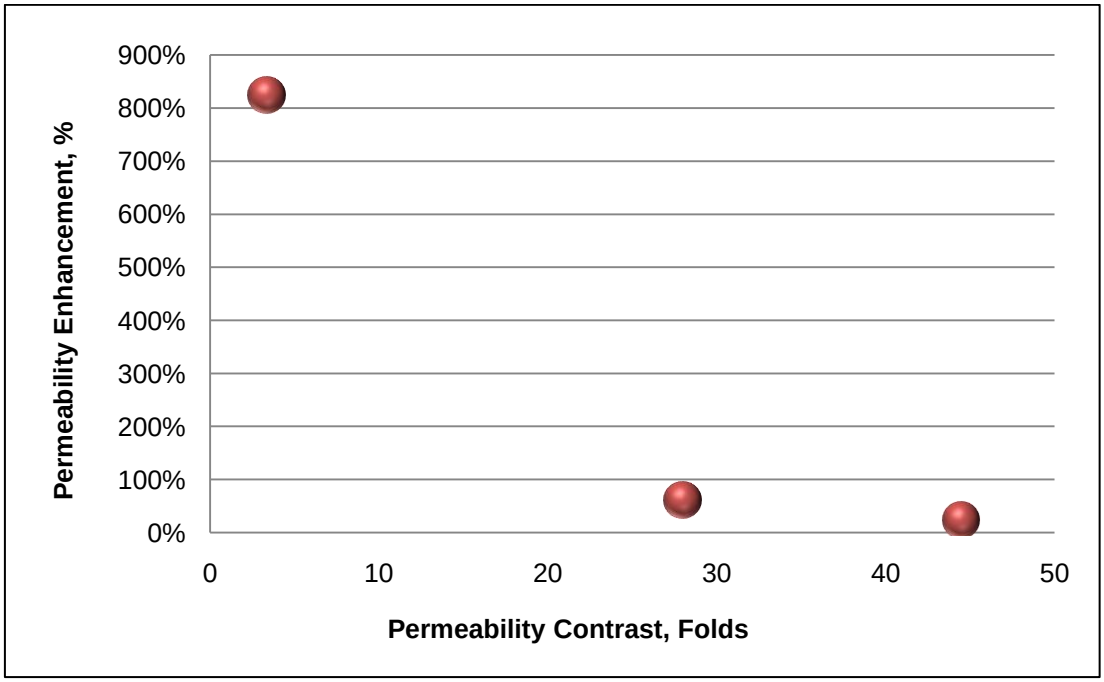

Figure 5.1.7: Diversion Enhancmenet with Contrast Effect Plot for VES acid system.

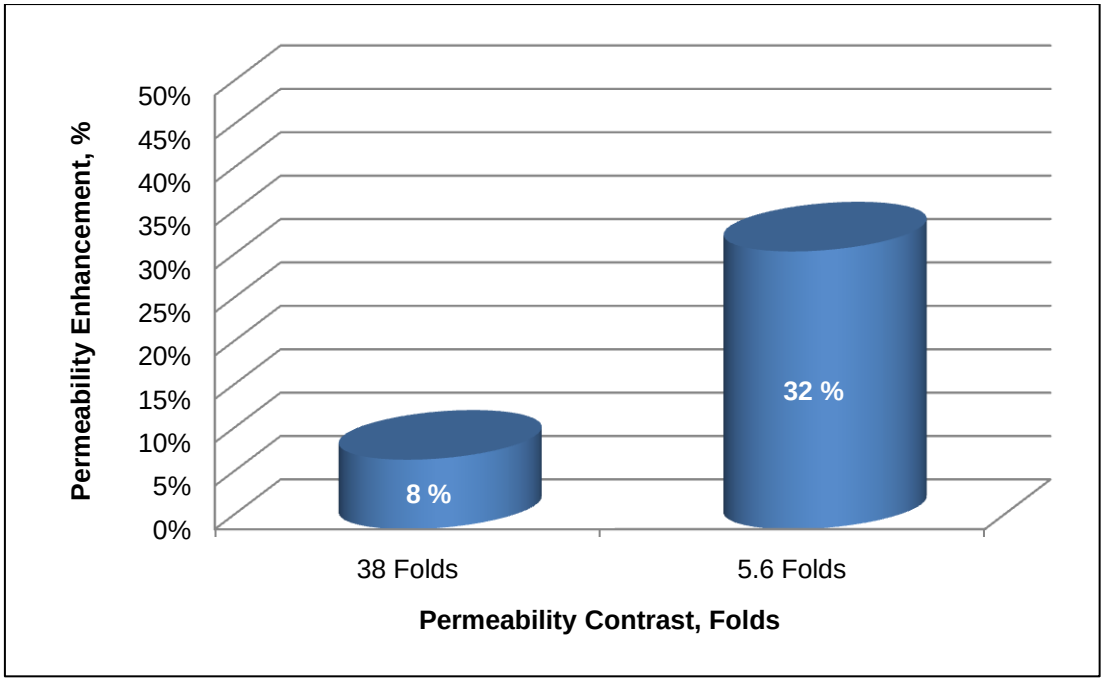

Figure 5.1.8: Permeability Contrast Effect on Diversion Efficiency of VES acid system using VES = 3.75%.

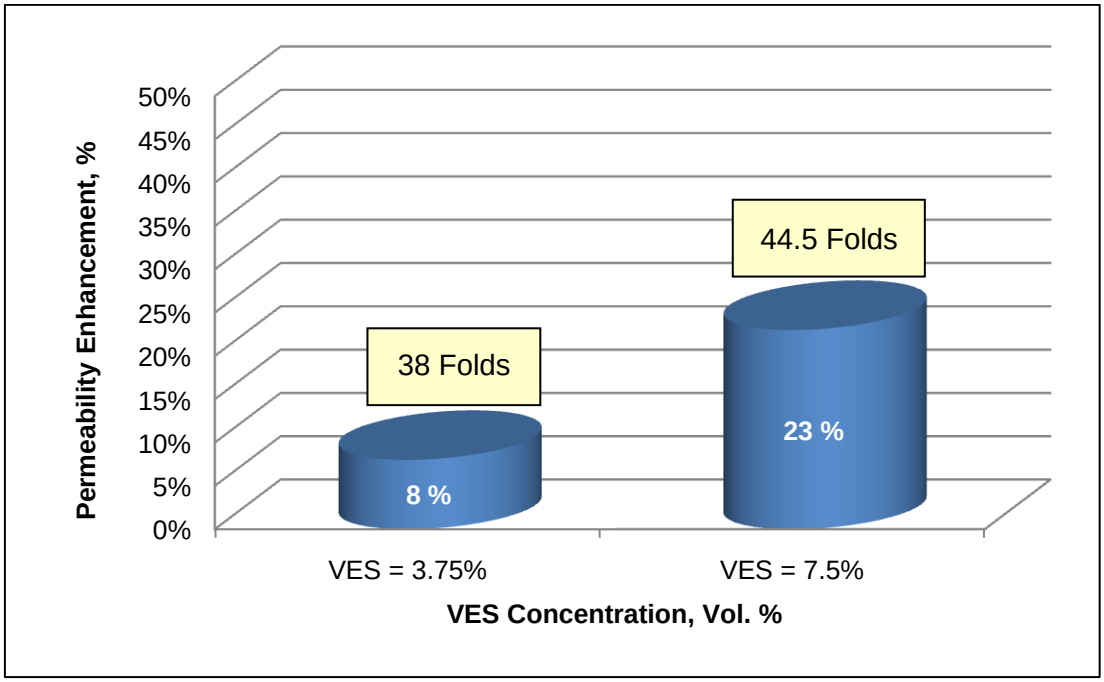

Figure 5.1.9: VES Concentration Effect on Diversion Efficiency of VES acid system.

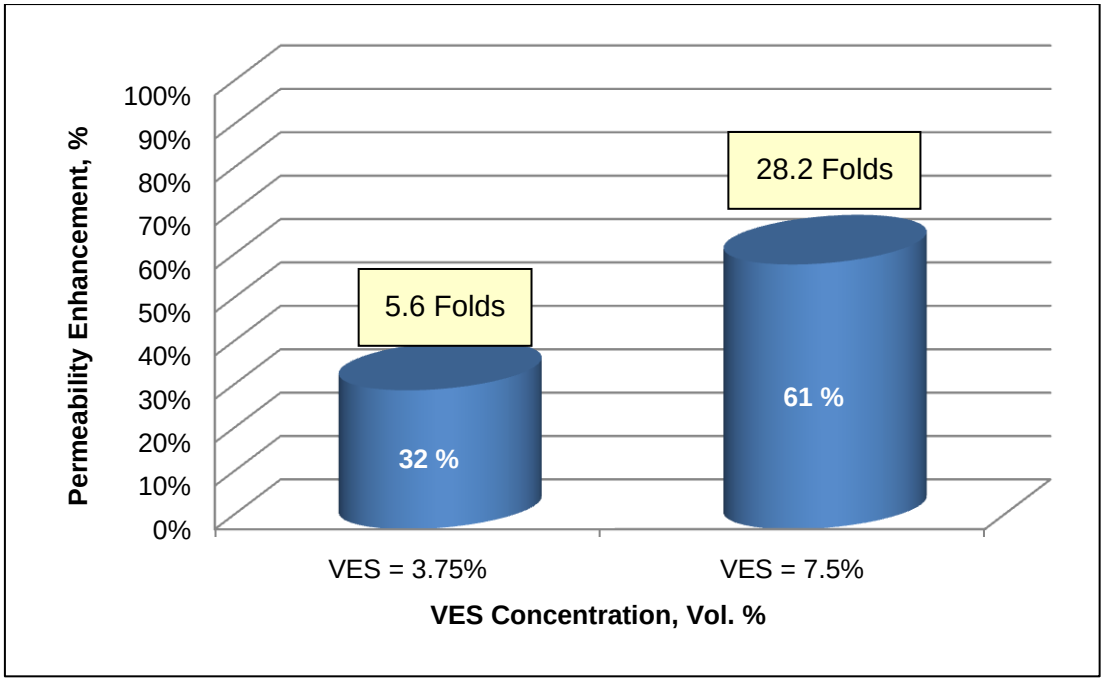

Figure 5.1.10: VES Concentration Effect on Diversion Efficiency of VES acid system.

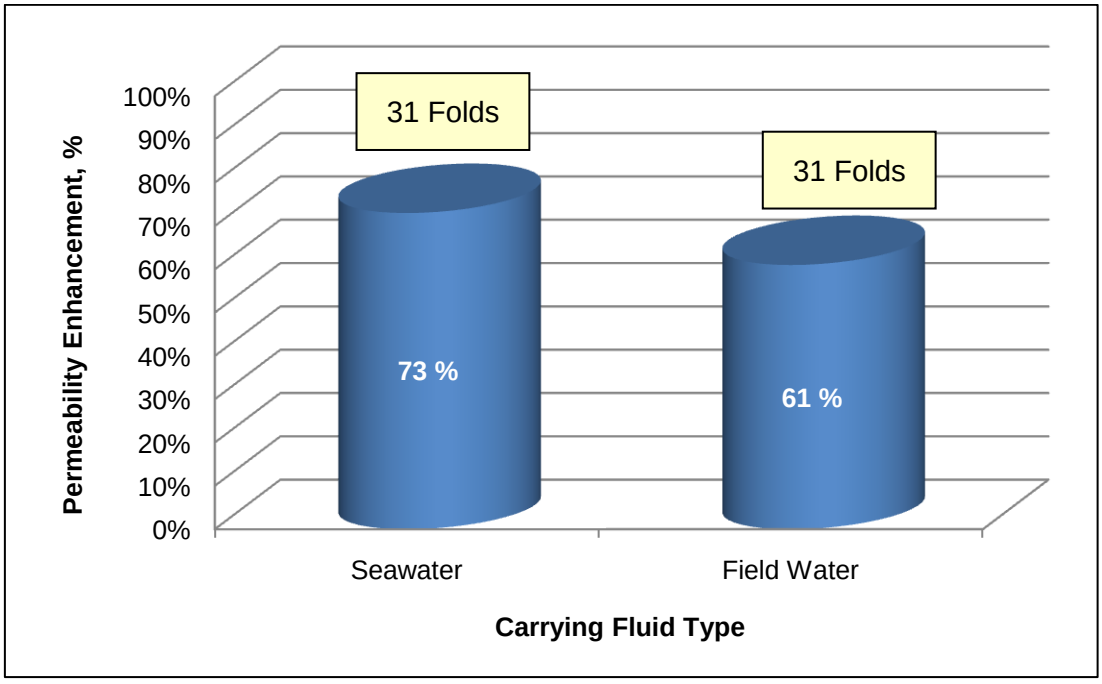

Figure 5.1.11: Mixing water Salinity Effect on VES acid system Diversion (3.75%), Seawater and Field Water.

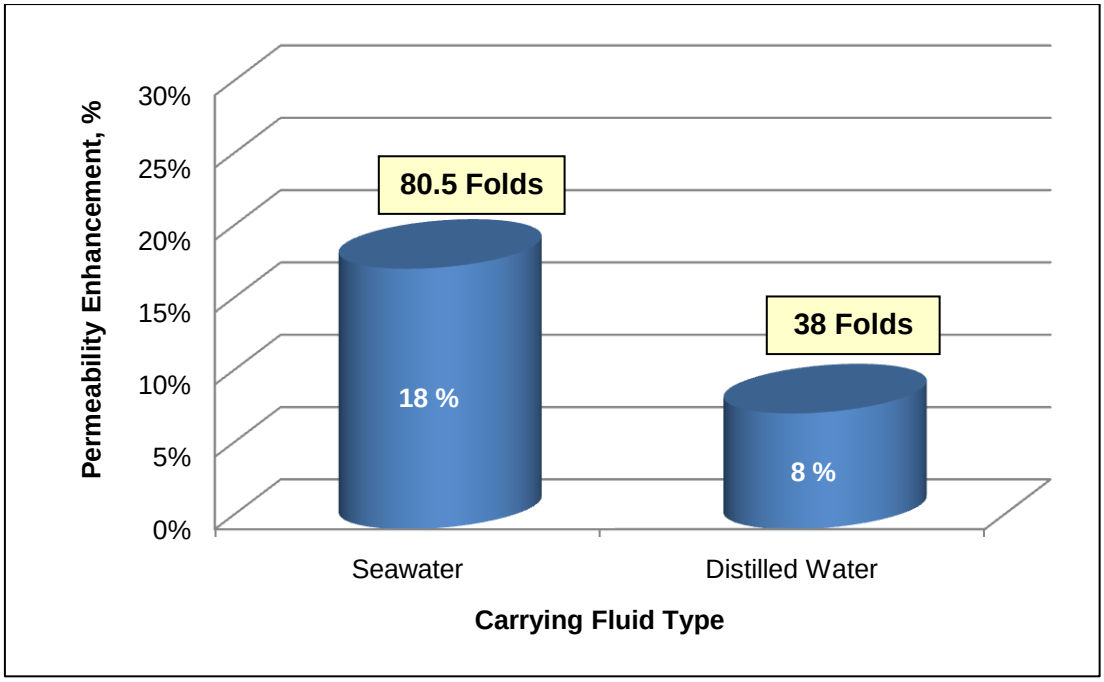

Figure 5.1.12: Mixing water Salinity Effect on VES acid system Diversion (3.75%), Seawater and Distilled Water.

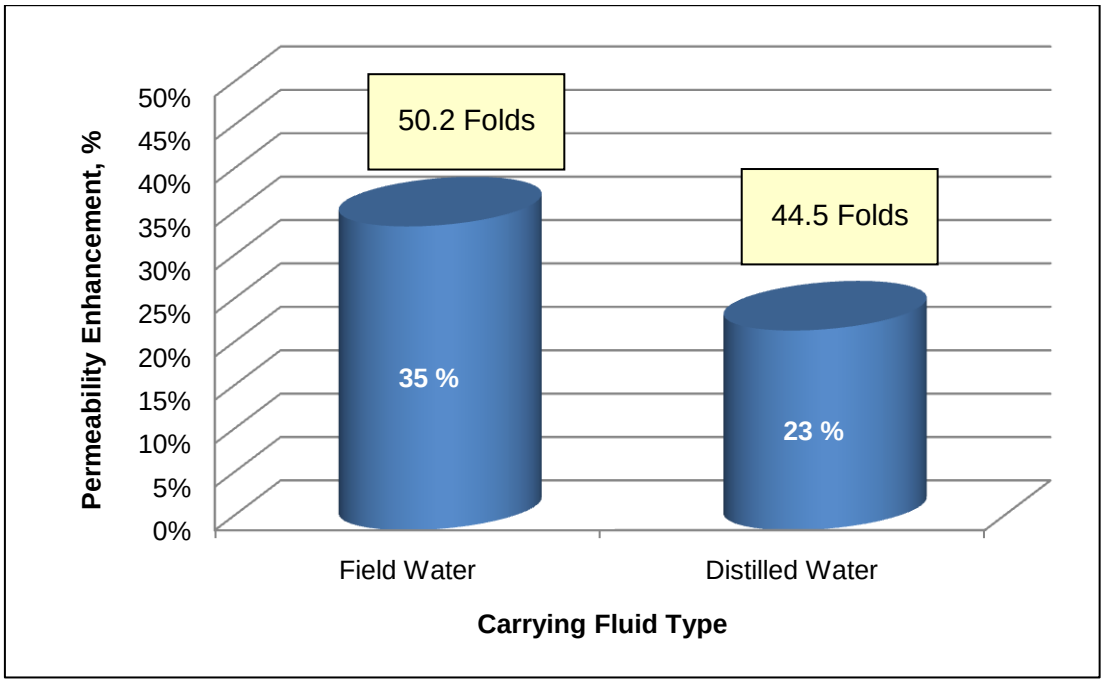

Figure 5.1.13: Mixing water Salinity Effect on VES acid system Diversion (7.5%), Field Water and Distilled Water.

5.2 Experimental Evaluation of Viscoelastic Surfactant Acid Diversion for Carbonate Reservoirs: Parameters and Performance Analysis

5.2.1 Abstract

Acid stimulation treatments are widely applied in the oil and gas industry to enhance the productivity of oil and gas wells and the injectivity of water injection wells. Viscoelastic surfactant (VES) acid treatments were used in the industry as a diversion system. The diversion efficiency of VES system was verified through lab studies conducted using parallel core flooding experiments which showed that the diversion efficiency of the VES-based acid system is dependent on several parameters such as water salinity, VES concentrations, and the permeability contrast of the core samples. This paper evaluates the effect of these parameters in addition to the influence of calcium chloride on the viscosity of spent and live HCl VES-based system. The viscosity results showed that these parameters have substantial effect on the system's viscosity. Also, the results offered an explanation to the observed trends in diversion efficiency shown in recent published literature. Also, the paper investigates the effect of temperature on the viscosity and diversion efficiency of live and spent HCl acid. Interesting viscosity behavior was observed at a VES concentration of 7.5% in the temperature range 80-150 ^{o}F where the viscosity increased with temperature. The effect of various parameters on the viscosity of spent and live HCl VES-based system was investigated. Also, the thermal stability of spent and live HCl VES based system was examined. The temperature effect on diversion was studied using core flooding equipment capable of flowing two parallel 9" long with a diameter of 3" carbonate core samples. A correlation between enhancement in viscosity due to salinity was correlated to diversion efficiency.

5.2.2 Introduction

Viscoelastic surfactants (VES) have shown effective performance as diverting materials for acid stimulation systems in carbonate reservoirs. This is attributed to the VES ability to significantly increase the viscosity as acid is spent within the formation which causes the fluid to divert to the low permeability zones. VES-based acid systems are polymer-free and solids-free systems; this feature makes them almost non-damaging compared to other chemical diverting techniques available in the industry (Nasr-El-Din et al., 2004). The viscosity of these systems is gained from the interaction between the acid reaction products (salts) and the VES molecules. With the rise of the pH of the acidic system above 2 and the increase in the concentration of the divalent cations (Ca^{2+} and Mg^{2+}) in the spent acid, the VES molecules form long worm-like micelles which cause the viscosity of the treatment fluid to increase dramatically. The increase in viscosity is a function of the concentration of the generated salts and the pH of the solution. **Figure 5.2.1** shows the mechanism of viscosifying the VES with increasing pH (Chang et al., 2001).

VES-based diverting acid system has low viscosity on the surface and in the wellbore but its viscosity increases significantly when it penetrates inside the carbonate reservoir. The viscosity is generated inside the formation as the acid component of the system reacts with the reservoir rock and generates salts. This increase in viscosity inside the reservoir matrix creates high pressure buildup resulting in slowing the treatment flow in the high permeability zones and, therefore, diverting the treatment flow to the lower permeability zones. In contrast to the VES-based diverted system, polymer-based diverted system is already viscous on surface and requires high pump pressure at high flow rate (Nasr-El-Din et al., 2008).

The high viscosity of the spent acid can be reduced and the well can be cleaned up after the treatment completion by either hydrocarbons contact during flow back or injection of a solvent. For water wells, solvents or mutual solvents can be used to break the viscosity of the system inside the formation. After the cleanup, the VES does not leave a residue in the formation as it will break into small spheres-shaped surfactants (4-10 nm in diameter) which can be easily flown back from the formation porous medium to the surface (Chang et al., 2001).

The purpose of this study is to evaluate the effect of various parameters on the viscosity of the spent and live 15% HCl VES based system. These parameters included mixing water salinity, effect of $CaCl_2$, VES concentration and spending 15% HCl acid evaluated at 150 ^{o}F (65.6^{o}C), 200^{o}F (93.3^{o}C), and 250^{o}F (121.1^{o}C). The viscosity measurements were compared to the results of the diversion efficiency from core flooding experiments in an attempt to correlate the two different measurements. The temperature effect on diversion efficiency and the viscosity of spent and live 15% HCl acid VES based system was also investigated. The thermal stability of spent and live 15% HCl VES based system was evaluated.

Recent studies showed that acid VES-based system rheology depends on several parameters. These parameters include acid concentration, temperature, dissolved salts concentration, pH, additives, and shear rate. As these parameters have impact on VES rheology, they are expected to have an effect on the diversion efficiency. The following sections demonstrate the previous research work conducted on the effect of some of these parameters on VES acid systems (Nasr-El-Din et al., 2007).

A thorough literature review indicated that the addition of $CaCl_2$ and NaCl salts has an increasing effect on the apparent viscosity of the VES system; the higher the concentration of these salts, the higher is the viscosity of the VES system. A recent study evaluated the effect of adding different calcium chloride concentrations on the viscosity of the VES acid system at room temperature and shear rate of 170 s^{-1}. The study showed that the viscosity increases significantly as the concentration of $CaCl_2$ increases in the mixing water. At VES concentration of 5 vol. %, the system viscosity increased from 30 to 80 mPa.s as the concentration of $CaCl_2$ increased from 4 to 5 wt.%. Also, it showed that at different VES concentrations, the impact of the salts concentration is different in magnitude. The salinity effect gets more significant as the concentration of the surfactant increases (Nasr-El-Din et al., 2007).

The addition of other types of salt, NaCl, showed the same trend observed by adding $CaCl_2$. A recent study showed that at a surfactant concentration of 5 vol.% and without adding NaCl, the viscosity is 15 mPa.s. When NaCl concentration is increased to 5 wt.%, the viscosity of the VES solution increased from 15 to 90 mPa.s. Increasing the salinity of mixing water is expected to lead to VES viscosity buildup which depends on salt concentration in the fluid (Nasr-El-Din et al., 2007).

The effect of VES concentration on the apparent viscousity of VES system is important as it will affect the pumping rates required for conducting the stimulation treatment. It was found from a recent study that the VES concentration has a significant effect on the viscosity at room temperature. A study conducted by Nasr-El-Din et al.,(2008) showed that at a concentration of 1 vol %, the viscosity was 12

mPa.s while at 7 vol%, the viscosity increased to 87 mPa.s. Therefore, up to a concentration of 7 vol.%, the increase in the viscosity of the VES system is propotional to concentration.

VES-based acid system undergoes different pH values when it is in contact with the reservoir rock. Initially, the pH is very low and eventually, it increases to 4 as HCl acid reacts with the rock and gets spent. The pH was found to be very critical to the gelation of the VES system even if a large amount of salt is generated and dissolved in the solution. A study was conducted to investigate this effect and it was found that below a pH of 1 the gelation is not significant but as the pH exceeds 2, the solution viscosity increases sharply. Usually when the VES solution is in the formation, the pH increases above 2 as a result of the acid reaction with the carbonate rock. This results in an increase in the viscosity of the solution in the presence of the generated salts (Chang et al., 2001).

The main objective of the VES acid system is to help to achieve a uniform stimulation treatment of the long horizontal section of a carbonate reservoir well. The effectiveness of the VES system as a chemical diverting system was evaluated in various studies and field cases. VES system has shown higher efficiency than other conventional acid-diverging systems. Oil production was compared in a field treated with conventional acid system and VES based acid system. An average of 1,600% more production resulted from wells treated with VES systems. In another field data, it was shown that VES diverging technique resulted in 4 to 5 folds increase in oil production compared to conventional methods (Chang et al., 2007).

In another study, higher concentration of acid was used to evaluate the efficiency of the diversion of VES system by Nasr-El-Din et al. (2006). Core samples of 1-inch in diameter by 2-inch in length were used in the study. The acid and VES concentrations were set at 28 wt. % and 4 Vol.%, respectively. The return permeability results showed an increase in permeability in both core samples. **TABLE 5.2.1** shows the summary of their core flooding results.

Recent lab studies of our group that used parallel core flooding experiments showed high efficiency of the VES system in diverting HCl acid. The study used 15% HCl VES based system and long carbonate core samples, 9" long and 3" in diameter. The core flooding results showed that the VES was able to stimulate the high permeable core as indicated by a breakthrough. Also, the VES had significantly stimulated the tight cores with 824% enhancement in permeability. The study has shown also that the diversion efficiency of the VES system is heavily dependent on the VES concentration, mixing water salinity, and permeability contrast of the core samples. **TABLE 5.2.2** shows the results of three core flooding tests conducted to verify the diversion efficiency of the VES-based acid system and the effect of permeability contrast on diversion (Al-Otaibi et al., 2011).

The previous studies investigated the effect of several parameters on the viscosity of the VES. These parameters include pH, $CaCl_2$, NaCl, and VES concentrations. These parameters were shown to have an increasing impact on the viscosity of the VES system. The diversion efficiency of the VES system was evaluated using carbonate core samples where 15% HCl VES based system showed effective stimulation of both samples in parallel. This shows the ability of the VES in diverting the acid from high

to low reservoir zones. Also, the core flooding studies indicated that the diversion efficiency of the VES system is greatly affected by the carrying fluid salinity, VES concentration, and core permeabilities or permeability contrast.

The impact of water salinity and VES concentration on the diversion efficiency of the acid VES system has not been investigated. In this study, experiments were performed to assess the impact of these two parameters on the viscosity to offer an explanation to the behavior noticed in the diversion efficiency results. The impact of temperature on the diversion efficiency is yet to be reported in the literature. In this study, core flooding tests were conducted at 150 ^{o}F (65.6 ^{o}C) and 200 ^{o}F (93.3 ^{o}C) to evaluate the effect of temperature on the performance of the VES system as a diverting agent. The thermal stability of the VES system in live and spent acid was also examined.

5.2.3 Experimental Procedure

5.2.3.1 Materials

Fluids

The VES used in this study is a zwitterionic type. The VES was used as a fresh sample with corrosion inhibitor added to HCl solution to prevent corrosion in the core flood lines. To investigate the effect of mixing water salinity, three water salinities were used in the study: distilled water; field water; and seawater. The seawater formulation used resembled that of the Arabian Gulf seawater. The field water was commonly used field water in Saudi Arabia for field operations. The chemical compositions of the distilled water, seawater and field water are shown in **TABLE 5.2.3**.

Indiana limestone cores were used in the core flooding experiments. Each sample had a length of 9” and a diameter of 1.5”. The chemical composition of the core sample used is shown in **TABLE 5.2.4**. Indiana limestone cores have a composition of 100% Calcite. The core samples used in this study and their permeabilities are listed in **TABLE 5.2.5**.

5.2.3.2 Sample Preparation

The fluids used in the experimental work were prepared using different mixing procedures depending on the additives. The following sections describe the mixing procedure of the experimental fluids. The brines used in the study were mixed at different formulations depending on the type of brine. The different brines used in the study were 3% KCl brine, Arabian Gulf seawater, and field water as shown in **TABLE 5.2.3**. The brines were mixed first using distilled water and then filtered through 0.3 micron filter paper before using them in the experiment. In this study, 15% HCl concentrations was prepared from 37% assay acid. The acid was mixed after preparing and filtering the brine. The mixing was conducted using a magnetic stirrer to ensure uniform mixing. Then, the corrosion inhibitor and the VES were added using a mixer to ensure homogeneity. The VES was added slowly to the mixture while mixing for 5 minutes. The resultant solution foamed due to the mixing process. The foaming mixture was then degassed by centrifuging for 5 minutes at 3,000 rpm. The formulation used to prepare the VES is shown in **TABLE 5.2.6**. Spent 15% HCl VES-based system was prepared in the same way except for adding equivalent produced amounts of $CaCl_2$ and H_2O as a result of the reaction of 15% HCl with $CaCO_3$. **TABLE 5.2.7** shows the formulation of spent 15% HCl VES-based system.

The amounts of produced $CaCl_2$ and H_2O added were calculated based on the reaction of HCl acid and $CaCO_3$ as shown in Equation-1. As indicated by equation (1), 2 moles of HCl react to produce one mole of $CaCl_2$ and one mole of H_2O. The density and molecular weights were then used to calculate how many grams of $CaCl_2$ and H_2O will be produced per mL of HCl. Equations (2) and (3) show the equations used to calculate the amounts of $CaCl_2$ and H_2O.

$$2\ HCl\ +\ CaCO_3 \quad ====>\quad CaCl_2 + CO_2 + H_2O \qquad (1)$$

Amount of $CaCl_2$:

$$(HCl\ reacted, mL)X\ \left(\frac{1.18\ X\ HCl, grams}{HCl, mL}\right)X\ \left(\frac{HCl, mole}{36.46\ HCl, grams}\right)X\ \left(\frac{CaCl_2\ mole}{2\ XHCl, moles}\right)X\left(\frac{111\ X\ CaCl_2, grams}{CaCl_2, grams}\right) \quad (2)$$

Amount of water:

$$(HCl\ reacted, mL)X\ \left(\frac{1.18\ X\ HCl, grams}{HCl, mL}\right)X\ \left(\frac{HCl, mole}{36.46\ HCl, grams}\right)X\ \left(\frac{H_2O\ mole}{2\ XHCl, moles}\right)X\left(\frac{18\ X\ H_2O, grams}{H_2O, grams}\right) \qquad (3)$$

5.2.3.3 Apparatus

Parallel Core Flood System

Parallel Core flood equipment was used to study the diversion efficiency of the VES based acid system. A schematic diagram of the core flood apparatus is shown in **Figure 5.2.2**. The core flood system was designed to flow through two cores in parallel. The apparatus consists of an oven, positive displacement pumps, accumulators, confining pump, two core holders, back pressure regulator, and data acquisition system. Each core holder can accommodate a core sample with a diameter of 1.5" and variable length. The core holders were placed inside a temperature-controlled forced-air circulation oven. The positive displacement pumps delivered a

consistent and continuous flow rate. Pressure transducers were used to measure pressure drop across the core samples. A back-pressure regulator was installed downstream of the core to control the pressure. Confining pump was used to keep a constant confining pressure on the core samples during the experiment. The confining pressure is used to apply an overburden pressure over the core samples simulating the reservoir rock pressure. Accumulators with floating pistons were used to store and inject fluids. The data acquisition software controls the variables of the experiment such as the fluid flow rate and flow direction. Experimental data was collected using an Excel sheet program installed in the software. A rotational viscometer was used to conduct the viscosity measurements. The viscometer is shown in **Figure 5.2.3**. It is a Chandler type with a sample volume of 54 cm^3. In order to avoid sample evaporation, the high pressure cell is sealed and connected to a nitrogen cylinder to allow the pressurization of the sample up to 300 psig.

5.2.3.4 Testing Procedure

This section describes the testing procedure for base permeability. The core samples were first placed inside the parallel core holders. Then, the confining pump was used to apply a confining pressure of 2,000 psig. The back pressure was set at 1,000 psig and the temperature of the oven was set at the desired temperature. After that, 3% KCl brine was injected at a flow rate of 2 mL/min through each mounted core sample until the steady state pressure drop across the core samples is reached. KCl was used to account for any possible clay present in the samples to eliminate clay swelling. Once the first sample reaches the steady state base permeability, the flow was switched to the other core sample for base permeability measurement. The pressure drop across the core sample was automatically recorded.

After establishing the base permeability for the mounted core samples, the fluid system was prepared according to the outlined procedure as shown in **TABLE 5.2.6.** Then, the fluid was loaded in the accumulators for injection. The injection rate was selected to be 5 mL/min. The flow rate was maintained until one of the core samples encountered a breakthrough where the pressure drop was almost zero. After that, the pump was stopped and the treatment was cleaned from the lines of the system. The treatment refers to the VES acid system fluid that's used to stimulate the core samples. While injecting the treatment, the pressure drop across the samples was automatically recoded. The return permeability is the permeability established after applying the treatment acid system. It was established by injecting the 3% KCl brine at 2 mL/min flow rate until a steady state pressure drop is reached across the core sample. The return permeabilities values were used to measure the enhancement of the treatment on the core sample. The permeability of the core sample in the base and return stages were calculated using Darcy's law. The enhancement of the treatment was calculated using the following equation.

$$K_{rp} = \frac{K_r}{K_b} \times 100 \quad \text{……...……..... (2)}$$

Where,

K_{rp} = Retained Permeability, % (Permeability Enhancement)

K_b = Bas Permeability, mD.

K_r = Return Permeability, mD.

The diversion efficiency of VES acid system was evaluated by measuring the retained permeability. For each core flood experiment, the obtained retained permeability value presents the enhancement of the tighter core sample as the higher permeability core sample had infinite retained permeability. The retained permeability was used to compare and rank the diversion efficiencies obtained for different core flood experiments. The higher the retained permeability the more efficient is the diversion.

5.2.4 Results and Discussion

5.2.4.1 Effect of Salinity on Spent VES-Based System Viscosity

The mixing water salinity was found from a recent study to have an effect on the diversion efficiency of 15% HCl acid based VES system. The study showed that using higher salinity will result in higher diversion efficiency as indicated by the enhancement in return permeability. Through parallel core flooding experiments, the study showed that stimulating 44.5 folds core samples using distilled water resulted in 23% enhancement in the tighter core sample. When field water was used, the enhancement increased to 35%. This was conducted using core samples with permeability contrast of 50.2 folds which makes it even harder to divert the acid than at 44.5 folds. The increase in enhancement at higher core contrasts shows the significant impact of salinity on the diversion efficiency of acid VES based system (Al-Otaibi, 2011).

The salinity effect on the diversion efficiency of acid VES-based system was attributed to the observed increase in viscosity as a result of increasing water salinity. In this section, the effect of increasing water salinity on spent acid VES-based system viscosity was evaluated by measuring the viscosity at different water salinities. To

simulate the spent acid, equivalent amounts of $CaCl_2$ were added to the solution of the VES system. **TABLE 5.2.7** shows the formulation of the spent acid used. The study evaluated the salinity effect at three concentrations of VES, 1 vol.%, 3.75 vol.%, and 7.5 vol.%. The temperature used in the viscosity measurements was 150 ^{o}F (65.6 ^{o}C) which is the same as the temperature in the previous core flooding experiments. The shear rate was set at a constant value of 40 s^{-1}.

The viscosity of spent acid system containing 7.5 vol.% VES was first evaluated using distilled water. The viscosity at 150 ^{o}F (65.6 ^{o}C) was 618 cP. When seawater was used, the viscosity increased to 800 cP. The results showed a proportional effect of salinity on the viscosity of spent acid VES based system. The increase was shown to be of a significant magnitude, 25%, as shown in **Figure 5.2.4**. Field water was not used at VES concentration of 7.5% vol.%.

Another set of tests were conducted to depict the effect of salinity using lower VES concentration, 3.75 vol.%. Distilled water and seawater were tested with an additional intermediate salinity, field water. The distilled water resulted in a viscosity value of 154 cP and the viscosity increased by 38% to 213 cP when field water was used. The viscosity increased by 22%, from 213 for field water to 261.5 cP when seawater was used.

The seawater resulted in a higher viscosity than both field water and distilled water. The trend obtained using 3.75 vol.% VES is similar to that of 7.5 vol.% VES. However, at 3.75% VES, the effect of salinity was shown to be higher in magnitude; **Figure 5.2.4** shows the results of the viscosity values generated for the spent acid containing 3.75% VES system. At 1% VES concentration, distilled water showed a

viscosity value of 16 cP. When field water and seawater were used, the viscosity increased to 27 and 38 cP, respectively. The obtained results show that increasing the salinity of spent acid system containing 1 vol. % VES increases the viscosity of the solution. The results are shown in **Figure 5.2.4**.

The generated results indicate that water salinity has a strong effect on the viscosity of spent acid in the concentration range 1-7.5 Vol.% VES. The increase in viscosity with salinity is attributed to the effect of the cations in the solution. In distilled water, the concentration of Ca^{2+} and Mg^{2+} are almost zero where their concentrations were 126 and 53 mg/L in field water, respectively. The concentrations of these ions are even higher in seawater. The seawater contains 592 and 2,304 mg/L of Ca^{2+} and Mg^{2+}, respectively. The presence of these ions in the solution will enable viscosity buildup. Therefore, the higher the concentration of these ions in the solution, the higher is the viscosity of the VES system.

The results also showed that viscosity increased at higher rate when the salinity was increased from distilled water to field water more than when the salinity was increased from field water to seawater. Hence, the increase in viscosity with increasing salinity was shown to be non-linear. There are two anticipated mechanisms that offer explanations to the observed behavior. The first explanation is that the viscosity increases with salinity at a high rate initially and then it reaches a plateau. Therefore, the effect of increasing the salinity from field to seawater is low compared to increasing the salinity from distilled water to field water. On the other hand, another possible explanation is that the viscosity of the VES system versus salinity goes through increase at low salinity followed by a decrease at intermediate salinities and finally another increase at higher salinities. This behavior is similar to the

behavior of polyelectrolyte solutions where the type and concentration of salt control the morphology of the VES micelles. However, the effect of salinity needs further investigation with respect to the influence of different salinities in the range of field to seawater. Also, the impact of the individual cations should be studied.

The salinity of the spent acid VES-based system showed significant impact on the viscosity of the solution. This trend was shown to be consistent over the three tested VES concentrations, 1 vol. %, 3.75 vol. %, and 7.5 vol. %. This finding provides an explanation to our previous results from the parallel core flooding study. The diversion efficiency of the VES based system showed increase as given in **TABLE 5.2.8**. The viscosity results generated in this section indicate that the reason behind the increase in diversion efficiency with salinity is the increase in viscosity due to the increase in salinity. Since viscosity is the key enabler behind VES system diversion, the additional viscosity offered at higher salinity causes the VES system to be more efficient in diverting the acid.

5.2.4.2 Effect of $CaCl_2$ on the Viscosity of VES System

The concentration of $CaCl_2$ in the acid VES based system is the main factor behind the increase in the viscosity of the VES system. $CaCl_2$ is produced from the reaction between the rock materials and the acid system where it mixes with the solution and helps the viscosity build up. In this section, the effect of $CaCl_2$ on the viscosity of VES system is measured at different VES concentrations. The effect of $CaCl_2$ on viscosity was investigated by measuring the viscosity of the VES system with and without $CaCl_2$. The amount of $CaCl_2$ added is equivalent to the produced amount upon spending the acid through the reaction with calcium carbonate materials. All viscosity

tests were performed at 150 ^{o}F (65.6 ^{o}C) and a shear rate of 40 s^{-1}. Two sets of experiments were conducted, at 7.5 and 3.75 vol% VES; the effect of $CaCl_2$ on the viscosity of spent acid VES-based system was evaluated first by using 7.5 vol.% VES. The viscosity of the 7.5 vol.% VES system without $CaCl_2$ was found to be 470 cP at 150 ^{o}F (65.6 ^{o}C). When $CaCl_2$ was added, the viscosity increased to 618 cP. The increase in viscosity represents 31.5%. The viscosity results are shown in **Figure 5.2.5**. The effect of $CaCl_2$ was also examined at lower concentration of VES, 3.75 vol.%. The viscosity of the 3.75 vol.% VES system without $CaCl_2$ was 100 cP. When $CaCl_2$ was added, the viscosity increased significantly to 261.5 cP which represents an increase of 161.5 % in the original viscosity of the VES system without $CaCl_2$. However, the drop in viscosity is ,in general, proportional to the drop in VES concentration. This observation is in agreement with the previous findings by Nasr-El-Din et al., 2008. So, the presence of VES leads to major increase in viscosity in comparison with VES-free solution but later increase is proportional to VES concentration. **Figure 5.2.5** shows these results.

The results observed by adding $CaCl_2$ to both 3.75 vol.% and 7.5 vol.% VES system showed remarkable increase in the viscosity. These results show the major role that $CaCl_2$ plays in increasing the viscosity of the acid VES based system when it gets in contact with the reservoir formation. $CaCl_2$ contains calcium cations, Ca^{2+}, which have strong interaction with the VES molecules. This interaction forces the surfactant molecules to align and form specific structures causing the viscosity to increase. Further investigation about the types of these structures and micelles is needed.

5.2.4.3 Effect of VES Concentration on the Viscosity of Spent 15% HCl VES-based System

The VES is the main diverting component of the acid VES based system. The effect of VES concentration on the diversion efficiency of the acid VES based system was evaluated by a recent study using parallel core flooding experiments. The study was conducted at 150 ^{o}F (65.6 ^{o}C) and showed that VES concentration has a substantial impact on the diversion efficiency of the acid VES based system. The study showed that increasing the VES concentration from 3.75 vol.% to 7.5 vol.% increased the diversion efficiency from 8% to 23% using core samples of permeability contrasts of 38 and 44.5 folds, respectively. The results are shown in **TABLE 5.2.9** (Al-Otaibi, 2011). The study explained the behavior through the role of VES in increasing the viscosity of the system. VES is responsible for increasing the viscosity of the VES acid system and therefore increasing its concentration will lead to a higher viscosity and, hence, better diversion.

This section studies the viscosity behavior of the spent acid VES based system at different VES concentrations, namely, 1 vol.%, 3.75 vol.%, and 7.5 vol.%. Also, the effect of VES concentration was evaluated for VES system alone. The study was conducted at different salinities using a shear rate of 40 s^{-1} and a temperature of 150 ^{o}F (65.6 ^{o}C). The effect of VES concentration on the viscosity of spent acid VES system was evaluated using three different salinities, seawater, field water, and distilled water. The tests were first conducted at 150 ^{o}F (65.6 ^{o}C). The viscosity results showed that increasing the VES concentration has a significant effect on increasing the viscosity of the spent 15% HCl acid VES based system. The trend was consistent over the different tested salinities.

For distilled water, the viscosity was 9 cP at 1 vol.% VES. When the VES concentration was increased above 1%, the viscosity showed steep increase. Increasing the VES concentration to 3.75 and 7.5 vol.% increased the viscosity from 9 cP to 154 cP and 618 cP, respectively. The same tests were conducted using field water and it showed the same trend. The viscosity increased from 27 to 213 cP when the VES concentration was increased from 1 to 3.75 vol.%. Therefore, this increase is not proportional to concentration. The VES concentration is suggested to pass through a critical micelle concentration that leads to the formation of networks (Hussein et at., 2010).

For the seawater, the VES concentration was found to have the highest impact on viscosity in comparison to distilled and field water. The viscosity at 1% VES concentration was shown to be 38 cP. At higher concentrations of 3.75 and 7.5 vol.% VES, the viscosity showed higher values of 261 and 800 cP, respectively. The results are shown in **Figure 5.2.6**. An interesting observation here is that the viscosity increase due to increasing the VES concentration varied depending salinity. Distilled water was shown to have the lowest change in viscosity where seawater showed the highest. This is attributed to the high concentrations of salts and cations contained in seawater.

The significant increase in viscosity was noticed when VES concentration was increased is attributed mainly to the formation of additional micelles. Increasing the concentration of VES will provide more VES molecules to be present in the solution. These molecules will form additional micelles that will hinder the movement of the

fluid and increase its viscosity dramatically. This increase was shown to be enhanced at higher water salinity which reflects the role of salts in enhancing the viscosity of the VES system.

This study evaluated the impact of VES concentration on the viscosity at higher temperatures, 200 ^{o}F (93.3 ^{o}C) and 250 ^{o}F (121.1 ^{o}C). The results showed the same increasing trend observed previously at 150 ^{o}F (65.6 ^{o}C); increasing VES concentration increased the solution viscosity at both temperatures over the three tested salinities, seawater, field water, and distilled water. Also, the viscosity increase at constant temperature was proportional to water salinity. Using higher salinity water, the concentration of VES showed more impact on the increase in viscosity than at lower salinity. The Results are shown in **Figures 5.2.7 & 5.2.8**. The results suggest that the presence of cations shifts the critical micelles concentration to lower values. At 7.5 vol.% VES, The slope of the viscosity curve is 9,842 cP/vol.% for seawater while it is 7322 cP/Vol.% for distilled water. At 3.75 vol.%, The slope of the viscosity curve is 36.53 cP/vol.% for seawater while it is 20.32 cP/Vol.% for distilled water

The diversion efficiency of the acid VES based system was shown earlier to be heavily dependent on the concentration of the VES in the solution. The previous results showed that the diversion efficiency increases drastically when the VES concentration is increased from 3.75 to 7.5 vol.%. The viscosity results generated in this section provide an explanation to the diversion efficiency results.

The previous section evaluated the impact of increasing VES concentration on the viscosity of spent HCl acid VES based system. This was attributed to the formation of

additional micelles due to the presence of more VES molecules. In this part of the study, another set of viscosity tests were conducted at 1, 3.75, and 7.5 vol.% VES concentrations without adding $CaCl_2$. $CaCl_2$ was removed to confirm that the high impact of increasing VES on viscosity was not only due to the VES alone but was mainly due to the formation of micelles due to the presence of $CaCl_2$. The tests were conducted using seawater at VES concentrations of 3.75 and 7.5 vol.%. The results were compared to assess the influence of $CaCl_2$ on the solution viscosity at difference VES concentrations.

The same trend was observed with the spent acid VES based system. The viscosity was 100 cP at 3.75 vol.% VES. When the VES concentration was doubled to 7.5 vol.% VES, the viscosity increased to 280 cP. This increase is more than the double which suggests that for distilled water, there exists a critical VES concentration between 3.75 and 7.5 vol.%. In the previous section, when $CaCl_2$ was added, the viscosity showed an increase from 261 to 800 cP indicating an increase of 539 cP above the original value. Both solutions showed an increase in viscosity as VES concentrations were increased from 3.75% to 7.5%. However, the solution that contained $CaCl_2$ showed higher increase in viscosity than the solution that contained VES only. This shows that the presence of $CaCl_2$ increased the formation of micelles. It was observed that almost the same viscosity which is achieved with 7.5 vol.% can be obtained with about half of this concentration in the presence of seawater. This shows that the use of salts and saline water can be utilized to reduce the amount of VES in the system and accordingly reduce the stimulation treatment cost.

5.2.4.4 Effect of Temperature on Diversion Efficiency

Carbonate reservoirs have different temperatures that can range from 130 ^{o}F (54.4 ^{o}C) to more than 200 ^{o}F (93.3 ^{o}C) depending on their depth and location. The field application of the VES system can be performed at high or low temperatures. The difference in temperatures in these reservoirs may have an impact on the diversion efficiency of the VES system as temperature is considered to be an important parameter that affects the viscosity of the VES system. The effect of temperature on the diversion efficiency of HCl acid VES based was not investigated before. It is of great interest to evaluate the impact of temperature on the diversion performance of the VES system. The experiments were conducted at 200 ^{o}F (93.3 ^{o}C) and the results were compared with our previous results at 150 ^{o}F (65.6 ^{o}C). 9" long carbonate core samples and 3" in diameter were used in the study. It is important to mention that the same set-up of equipment and experimental parameters were used in this test to have comparable results. As we mentioned earlier, the lowest contrast folds used was 3.4 and it showed a diversion efficiency of 824%. This implies that the higher permeability core sample was completely stimulated while the tighter core sample was partially stimulated with an enhancement in its original permeability of 824%. This experiment was conducted at a temperature of 150 ^{o}F (65.6 ^{o}C).

The base permeability was first established by using brine and then 15% HCl acid VES based system was injected simultaneously in the two core samples while the temperature was set at 200 ^{o}F (93.3 ^{o}C). Then, return permeability tests were conducted using brine to measure the enhancements in both core samples. The higher permeability core sample (sample-2) showed an infinite return permeability enhancement as a breakthrough was encountered. The tighter core sample (sample-1)

showed a return permeability value of 1.31 mD indicating an enhancement of 37%. Although a diversion was achieved as shown by the enhancement in the return permeability, the diversion efficiency is considered to be significantly low when compared to the diversion achieved at 150 ^{o}F (65.6 ^{o}C). Results are shown in **Figure 5.2.9**.

The generated results indicate clearly that temperature has a significant impact on the diversion efficiency of the VES system. Increasing the temperature from 150 ^{o}F (65.6 ^{o}C) to 200 ^{o}F (93.3 ^{o}C) reduced the viscosity of the VES system and accordingly hindered the ability of the VES system for diverting.

The core flooding results indicate that the diversion efficiency of the VES system is heavily dependent on the reservoir temperature. It is therefore important to verify that VES system can divert at high efficiency at the targeted field reservoir temperature. More optimization could be utilized to compensate for temperature effect such as increasing the VES concentration or the water salinity.

5.2.4.5 Temperature Effect on the Viscosity of the VES System

The performance of VES system in diverting HCl acid was shown to be a strong function of temperature. This was shown through the significant reduction in the diversion efficiency of the acid VES based system when the temperature was increased from 150 ^{o}F (65.6 ^{o}C) to 200 ^{o}F (93.3 ^{o}C). This section will focus on studying the viscosity of live and spent acid VES based system at different temperatures, water salinities, and VES concentrations. The mixing waters used in the study were seawater, field water, and distilled water. Three VES concentrations were

used in the study, 1, 3.75, and 7.5 vol.%. The temperatures used to measure the viscosity were 150 ^{o}F (65.6 ^{o}C), 200 ^{o}F (93.3 ^{o}C), and 250 ^{o}F (121.1 ^{o}C).

The impact of temperature on the viscosity of spent acid VES based system was measured at 150 ^{o}F (65.6 ^{o}C), 200 ^{o}F (93.3 ^{o}C), and 250 ^{o}F (121.1 ^{o}C). Results are shown in **Figure 5.2.10**. The first set of tests were conducted using 7.5 vol.% VES. The viscosity of distilled and seawater systems were initially high at 150 ^{o}F (65.6 ^{o}C) then it dropped at 200 ^{o}F (93.3 ^{o}C) and 250 ^{o}F (121.1 ^{o}C). For seawater, the viscosity at 150 ^{o}F (65.6 ^{o}C) was 800 cP and it decreased to 262 and 195 cP when the temperature was increased to 200 ^{o}F (93.3 ^{o}C) and 250 ^{o}F (121.1 ^{o}C), respectively. the viscosity-temperature relationship for distilled and seawater spent acid systems was fitted to Arrhenius behavior, $y=Ae^{E/RT}$, where y is the viscosity of the system, Pa.s., E is the fluid activation energy, J/mol and T is in the absolute temperature, K.

Distilled water showed the same behavior as seawater. The viscosities of the spent acid VES based system at 150 ^{o}F (65.6 ^{o}C), 200 ^{o}F (93.3 ^{o}C), and 250 ^{o}F (121.1 ^{o}C) were found to be 618, 180, and 175 cP. The results of the viscosity followed Arrhenius behavior and the flow activation energy was calculated as shown in **TABLE 5.2.10**. The results are plotted in **Figure 5.2.10-a, b,** and **c**. The results suggest that at high VES concentration, the influence of VES dominates over the influence of salinity. However, at intermediate concentrations, the impact of VES on both activation energy and pre-exponent is quite obvious.

The significant loss in the viscosity of the spent acid VES based system at higher temperatures offers an explanation to the decrease in the diversion efficiency

observed in the previous core flooding experiments. The VES acid system depends mainly on the generated viscosity to divert HCl acid from the higher to the lower permeability core sample. At 150 ^{o}F (65.6 ^{o}C), the viscosity was found to be more than three times the viscosity measured at 200 ^{o}F (93.3 ^{o}C) regardless of the water salinity.

This indicates that at 150 ^{o}F (65.6 ^{o}C), reservoirs treated with VES system are more likely to have better diversion and therefore higher productivity results than reservoirs at 200 ^{o}F (93.3 ^{o}C) and 250 ^{o}F (121.1 ^{o}C). Also, the results suggest that field application success achieved in reservoirs at 200 ^{o}F (93.3 ^{o}C) is likely to be achieved at 250 ^{o}F (121.1 ^{o}C) with slightly lower efficiency. This is due to the minor decrease in viscosity encountered from 200 ^{o}F (93.3 ^{o}C) to 250 ^{o}F (121.1 ^{o}C). For both distilled and seawater, the decrease in viscosity when the temperature was increased from 200 ^{o}F (93.3 ^{o}C) to 250 ^{o}F (121.1 ^{o}C) was 3 - 27 %.

The diversion efficiency of the acid VES based system is expected to be lower when the temperature was increased from 150 ^{o}F (65.6 ^{o}C) to 200 ^{o}F (93.3 ^{o}C). however, there are other parameters that could be optimized to increase the diversion efficiency. These parameters include water salinity and VES concentration. These two parameters were found to have significant impact on the viscosity.

Further, VES concentrations of 1% and 3.75% were used with seawater and distilled water. The viscosity values at both VES concentrations showed a decreasing trend as temperature was increased from 150 ^{o}F (65.6 ^{o}C) to 250 ^{o}F (121.1 ^{o}C). The results obtained had the same trend observed at 7.5 vol. % VES.

At 3.75% VES, increasing the temperature from 150 ^{o}F (65.6 ^{o}C), 200 ^{o}F (93.3 ^{o}C), and to 250 ^{o}F (121.1 ^{o}C), the viscosity of the seawater solution decreased from 261.5 cP, 165 cP, to 139 cP, respectively. For distilled water, the viscosity in this range showed higher sensitivity to temperature. The viscosity decreased from 154 cP at 150 ^{o}F (65.6 ^{o}C) to 24 cP at 200 ^{o}F (93.3 ^{o}C) and at 250 ^{o}F (121.1 ^{o}C) the viscosity was 6 cP only.

At 1% VES, the viscosity decreased following the same trend. For seawater, the viscosity was 38 cP at 150 ^{o}F (65.6 ^{o}C) and when the temperature was increased to 250 ^{o}F (121.1 ^{o}C), the viscosity drops to 21 cP. Increasing the temperature further to 250 ^{o}F (121.1 ^{o}C) decreased the viscosity to 15 cP. For distilled water, the viscosity values were 16, 9, and 4 cP at 150 ^{o}F (65.6 ^{o}C), 200 ^{o}F (93.3 ^{o}C), and 250 ^{o}F (121.1 ^{o}C), respectively.

Lower temperatures were used to evaluate the effect of temperature on the viscosity of spent 15% HCl acid containing 7.5% vol. VES using different mixing waters. The temperatures used to measure the viscosity were 70 ^{o}F (21.1 ^{o}C), 110 ^{o}F (43.3 ^{o}C), 150 ^{o}F (65.6 ^{o}C), and 200 ^{o}F (93.3 ^{o}C). For distilled water, the viscosity was found to be 311 cP at 70 ^{o}F (21.1 ^{o}C) and increased to 368 cP and 620 cP at 110 ^{o}F (43.3 ^{o}C) and 150 ^{o}F (65.6 ^{o}C), respectively. When the temperature was increased to 200 ^{o}F (93.3 ^{o}C), the viscosity decreased dramatically to 190 cP. For seawater, the same trend was observed. The initial viscosity was 356.5 cP and a peak of 810 cP was observed at 150 ^{o}F (65.6 ^{o}C) before it dropped to 263 cP at 200 ^{o}F (93.3 ^{o}C). The results are shown in **Figure 5.2.11** and **5.2.12**.

The viscosity increased as the temperature was increased from 70 ^{o}F (21.1 ^{o}C) to 150 ^{o}F (65.6 ^{o}C). When the temperature was increased above 150 ^{o}F (65.6 ^{o}C), the viscosity dropped significantly. This shows that the spent VES based system has a maximum viscosity at a certain temperature within this range where the viscosity above and below this temperature is lower than the peak value. This behavior suggests that the VES system will be more efficient to be applied at reservoirs with temperature of about 150 ^{o}F (65.6 ^{o}C) than at reservoirs with higher and lower temperatures. The increase of viscosity with temperature is unusual and usually observed in structured fluids. Hence, the temperature is suggested to play a role in building structures within the electrolyte solutions that leads to increased viscosity. A tentative explanation could be an increase in the micelle size due to increased mobility and contact of smaller micelles. Another possible explanation is a change in the type of morphology of the micelles.

The viscosity of the spent acid VES based system was found to be heavily dependent on temperature and was shown to have a maximum viscosity within the studied range. In this section, the temperature effect on live HCl acid containing 7.5 vol.% VES was evaluated using distilled water and seawater. The viscosity was measured at the same set of temperatures used in the previous section, 70 ^{o}F (21.1 ^{o}C), 110 ^{o}F (43.3 ^{o}C), 150 ^{o}F (65.6 ^{o}C), and 200 ^{o}F (93.3 ^{o}C). The initial viscosity for distilled water VES solution was 60 cP at 70 ^{o}F (21.1 ^{o}C). Then, the viscosity increased to 173 and 310 cP when the temperature was increased to 110 ^{o}F (43.3 ^{o}C) and 150 ^{o}F (65.6 ^{o}C), respectively. When seawater was used, the same behavior was observed where the viscosity increased with temperature up to 150 ^{o}F (65.6 ^{o}C) and then a sharp decrease in viscosity was obtained. The results are shown in **Figure 5.2.11** and **5.2.12**.

The viscosity results generated over the whole temperature range showed that both spent and live acid VES based system have the same trend where there is a maximum viscosity at a specific temperature. The results also showed that the temperature had initial unusual positive effect on the viscosity of the VES system up to a specific temperature where the viscosity of the system starts to decrease with temperature.

5.2.4.6 Effect of Spending HCl Acid on VES System Viscosity

In this section, the increase in viscosity was measured before and after spending the acid to evaluate the increase in viscosity gained after the treatment is spotted in the reservoir. The study was conducted using distilled water and seawater and the impact was evaluated at different temperatures, 70 ^{o}F (21.1 ^{o}C), 110 ^{o}F (43.3 ^{o}C), 150 ^{o}F (65.6 ^{o}C), and 200 ^{o}F (93.3 ^{o}C).

For seawater, the viscosity of the live acid with 7.5 vol.% VES was shown to be 60, 173, 310, and 9 cP at 70 ^{o}F (21.1 ^{o}C), 110 ^{o}F (43.3 ^{o}C), 150 ^{o}F (65.6 ^{o}C), and 200 ^{o}F (93.3 ^{o}C), respectively. After the acid is spent, the viscosity at these temperatures has increased sharply to 311, 368, 620, and 190 cP, respectively. The increase in viscosities at these temperatures due to the acid reaction was significant and ranged from 113% to 418% for temperatures in the range 70 ^{o}F (21.1 ^{o}C) to 150 ^{o}F (65.6 ^{o}C). **Figure 5.2.10** shows the increase in viscosity at different temperatures and **Figure 5.2.12** shows the increase in viscosity at the first three temperatures. When seawater was used, the same trend was observed where the viscosity was significantly increased upon spending the acid VES solution. The results are shown in **Figure 5.2.11** and **5.2.13**.

5.2.4.7 Thermal Stability of Live and Spent Acid VES System

Some viscous fluids lose their ability to retain their viscosities when the temperature is increased. This is usually verified through conducting thermal stability tests where the fluid's viscosity is measured at lower temperature and measured again at the same temperature after experiencing a rise in the temperature. If the viscosity is not retained at lower temperature, the fluid is considered thermally unstable. This section studies the thermal stability of live and spent acid VES based system. The viscosity was measured after step change in temperature of 50 ^{o}F. In both systems, 7.5 vol. %VES was used to investigate the stability of the VES system.

Spent acid with 7.5% vol. VES solution was first prepared and its viscosity was measured while heating the sample from 150 ^{o}F (65.6 ^{o}C) to 250 ^{o}F (121.1 ^{o}C). The viscosity was measured at 150 ^{o}F (65.6 ^{o}C) and 200 ^{o}F (93.3 ^{o}C) which showed values of 800 cP and 262 cP, respectively. Then, the solution was heated to 250 ^{o}F (121.1 ^{o}C) and its viscosity was 192 cP. After that, the solution was cooled back to 200 ^{o}F (93.3 ^{o}C) and 150 ^{o}F (65.6 ^{o}C) and its viscosity was measured at both temperatures and found to be 242 and 652 cP, respectively. While heating the sample to 250 ^{o}F (121.1 ^{o}C), the viscosity readings generated at 150 ^{o}F (65.6 ^{o}C) and 200 ^{o}F (93.3 ^{o}C) were shown to be higher than the values generated while cooling the sample from 250 ^{o}F (121.1 ^{o}C) to 200 ^{o}F (93.3 ^{o}C) and 150 ^{o}F (65.6 ^{o}C). This suggests that the VES solution is not stable at 250 ^{o}F (121.1 ^{o}C) and this observation could be attributed to the degradation of the VES.

The viscosity results showed that the solution did not maintain its original viscosity at 150 ^{o}F (65.6 ^{o}C) and 200 ^{o}F (93.3 ^{o}C). This is shown by the viscosity loss at both

temperatures. At 150 ^{o}F (65.6 ^{o}C), the solution showed a reduction of 8% in viscosity while at 200 ^{o}F (93.3 ^{o}C), it showed a reduction of 18.5%. These results indicate that the spent acid VES based system is thermally unstable. The results are shown in **Figure 5.2.14**.

The thermal stability of live acid VES solution was evaluated in the range of 110 ^{o}F (43.3 ^{o}C) - 200 ^{o}F (93.3 ^{o}C). The temperature was then reduced to 150 ^{o}F (65.6 ^{o}C) and then to 110 ^{o}F (43.3 ^{o}C). The viscosity was measured during the heating and cooling. While heating the sample, the viscosity was 173 and 310 cP at 110 ^{o}F (43.3 ^{o}C) and 150 ^{o}F (65.6 ^{o}C), respectively. The sample was heated further to 200 ^{o}F (93.3 ^{o}C) where its viscosity collapsed to 9 cP. On the other hand, while cooling the sample, the viscosity increased to 65 cP at 150 ^{o}F (65.6 ^{o}C). When the sample was further cooled to 110 ^{o}F (43.3 ^{o}C), the sample viscosity remained the same at 65 cP.

The thermal stability results showed that the live acid VES based system is not thermally stable as it has lost 79% of its viscosity at 150 ^{o}F (65.6 ^{o}C) and 63% of its viscosity at 110 ^{o}F (43.3 ^{o}C). The viscosity loss for live acid system was higher than the viscosity loss for the spent acid VES based solution. These results are shown in **Figure 5.2.15**. This dictates that the degradation of the VES is slowed by the presences of salts. This observation requires further investigation.

To further confirm the strong reduction in viscosity is not due to the long thermal exposure during viscosity measurements at 70 ^{o}F (21.1 ^{o}C), 110 ^{o}F (43.3 ^{o}C), and 150 ^{o}F (65.6 ^{o}C) prior to 200 ^{o}F (93.3 ^{o}C), another experiment was conducted where the sample was heated directly to 200 ^{o}F (93.3 ^{o}C). The viscosity started to decrease

dramatically from the time the sample reached 200 ^{o}F (93.3 ^{o}C) showing the same results obtained in the thermal stability test. The graph is shown in **Figure 5.2.16**. This suggests the thermal degradation of the VES.

5.2.4.8 Reflection on the results

The results shown in this study highlighted the effect of major field parameters on the optimization of the VES system application. For water salinity, the study showed that with higher salinity, the viscosity of the VES system increases which is desired to achieve better acid diversion and, hence, higher oil or gas production rates are obtained. Therefore, it is recommended to use higher salinity such as seawater and not consume the aquifer water for stimulation jobs or increase the cost of the stimulation job by using purer water. Further, the preliminary results of our study suggest that the presence of salts helps in slowing the degradation of the surfactant.

The other parameter that is examined in this study is the VES concentration. The study used typical field value for VES concentration which is 7.5% vol. Also, we evaluated two other lower concentrations, 1 and 3.75 vol.%. The results indicate clearly that lowering the concentration from 7.5 to 3.75 or 1 vol.% reduces the viscosity significantly which in turn reduces the diversion efficiency as shown from the reported results. From these results it is shown that 7.5 vol.% is desired to be used in the field, however, there is still some room for enhancement of diversion efficiency by increasing water salinity; hence, the VES concentration can be reduced. Such optimization of VES concentration requires a separate investigation.

The temperature effect on the diversion efficiency was significant. Increasing the temperature from 150 ^{o}F (65.6 ^{o}C) to 200 ^{o}F (93.3 ^{o}C) resulted in a decrease in the diversion from 824 to 37 %. As reservoirs' temperatures differ from one area to another based on their depth and location, it is important to consider this factor. Therefore, the system formulation should be optimized for the targeted reservoir temperature. At higher reservoir temperatures above 150 ^{o}F (65.6 ^{o}C), higher VES concentration and water salinity are recommended to overcome the temperature effect.

The thermal stability of the VES system showed that the system didn't retain its original viscosity when heated to higher temperatures. This is likely attributed to chemical breaking since enough time was allowed for micelle formation. Therefore, it is important to not preheat the VES system to higher temperatures before application in the well for stimulation as it may lose its ability to build viscosity.

Spending the VES acid system showed major increase in the viscosity, around 4 times at some conditions. This shows the viscosity difference between the system fluid pumped at the surface and the system fluid after it is spent inside the reservoir. This increase is important to have in the stimulation job since the field operations need lower fluid viscosity fluid at the surface to ease the pumping and save more pumping cost and higher fluid viscosity fluid in the wellbore to divert the acid.

5.2.5 Conclusions

This study explored the impact of several parameters on the viscosity of both live and spent HCl acid VES based system and their relationship to the diversion efficiency of the system. Based on the obtained results, the following conclusions can be drawn:

1. The water salinity showed strong impact on the viscosity of spent HCl acid VES based system. Increasing the salinity of mixing water from distilled water to seawater increased the viscosity by 30 – 69 % depending on the concentration of the VES.
2. $CaCl_2$ showed strong effect on increasing the viscosity of the VES system (31.5% - 116%).
3. The viscosity of the spent HCl acid VES based system was heavily dependent on the concentration of the VES; it showed an increasing trend with concentration.
4. The temperature had a significant impact on both the viscosity of the VES system and the diversion efficiency. The viscosity reduced from 800 to 192 cP when the temperature was increased from 150 ^{o}F (65.6 ^{o}C) to 250 ^{o}F (121.1 ^{o}C). Increasing the temperature from 150 ^{o}F (65.6 ^{o}C) to 200 ^{o}F (93.3 ^{o}C) reduced the diversion efficiency significantly from 824% to less than 37%. In the range of 70 ^{o}F (21.1 ^{o}C) to 150 ^{o}F (65.6 ^{o}C), the temperature was found to have an increasing effect on the viscosity of both spent and live 15% HCl VES based system.
5. Viscosity and diversion efficiency results imply that field application success rate of VES system is dependent on the targeted reservoir temperature.
6. Spending acid in VES system showed large increase in the viscosity of the VES based system ranging from 76% to 418% depending on the VES concentration and temperature.

7. Spent and live HCl acid VES based system was thermally unstable as it could not retain its original viscosity when heated at elevated temperatures.
8. VES concentration and salinity can be adjusted to provide a specific viscosity for a specific reservoir temperature.

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TABLE 5.2.1: Initial and final permeabilities of two core plugs used in parallel flow testing. The test was performed at 150 ^{o}F (65.6 oC) with 28 wt.% HCl and 4 vol.% surfactant [Nasr-El-Din et al., 2006]

Core Number	Initial Permeability (mD)	Regained Permeability (mD)
20	38	3,007
24	68	2,644

TABLE 5.2.2: Core flooding results of evaluating the diversion efficiency of acid VES based system using different core samples folds [Al-Otaibi et al., 2011]

Experiment Number	Core Sample #	Initial Permeability, (mD)	Permeability Contrasts, Folds	Enhancement, %
1	1	0.58 mD	3.4 Folds	824 %
	12	2.00 mD		Infinity
2	11	1.45 mD	28.2 Folds	61 %
	25	40.91 mD		Infinity
3	4	0.7 mD	44.5 Folds	23 %
	21	31.25 mD		Infinity

TABLE 5.2.3: Field water and seawater chemical analysis [Al-Muntasheri et al., 2007]

Variable	Distilled Water	Field Water	Seawater
Ca	< 1	126	592
Mg	< 1	53	2,304
Na	< 10	228	19,325
K	< 10	14	730
Cl	< 1	361	31,106
SO4	< 1	233	4,108
HCO3	< 1	171	183
TDS	---	1,186	58,348
pH	8.1	7.8	7.9
All Concentrations are in mg/l Total dissolved Solids (TDS) were determined by addition			

TABLE 5.2.4: Chemical Composition and Weight Percentage Compounds, Weight Percentage (Wt.%)

	Indiana Limestone
Calcite [CaCO3]	100
Dolomite [CaMg(CO3)2]	0

TABLE 5.2.5: Permeability Ranges of Core Samples used in the Parallel Core Flooding Experiments

Sample Number	Permeability, mD
1	0.96
2	2.68
3	2.00
4	0.58

TABLE 5.2.6: Live 15% HCl VES-based acid system formulation

Component	Amount
HCl	15 vol.%
VES	7.5 vol.%
Corrosion Inhibitor	0.6 vol.%
Mixing water (D.W., field water, or seawater)	76.9 vol.%

TABLE 5.2.7: Spent 15% HCl VES based acid system formulation

Component	Amount
$CaCl_2$	254.9 grams
VES	26.3 mL
Mixing water (D.W., field, or seawater)	365.1 mL

TABLE 5.2.8: Mixing Water Salinity Effect on VES acid system diversion [Al-Otaibi et. Al. 2011]

Carrying Fluid	Permeability Enhancement, %	Permeability Contrast, Folds
Seawater	73%	31
	18%	80.5
Field Water	61%	31
Distilled Water	8%	38

TABLE 5.2.9: VES concentration effect on VES acid system diversion [Al-Otaibi et. Al. 2011]

VES Concentration, Vol.%	Permeability Enhancement, %	Permeability Contrast, Folds
3.75	32	5.6
	8	38
7.5	61	28.2
	44.5	44.5

TABLE 5.2.10: Arrhenius equations parameters for the viscosity and temperature relationship at different VES concentrations and water types.

VES Concentration, vol.%	**Water Type**	**A**	**E,** J/mol	$y = A \times e^{E/RT}$
7.5	Seawater	2.0E-05	29,234	$y = 2E\text{-}05e^{3516.2(1/T)}$
	Distilled Water	5.0E-05	26,154	$y = 5E\text{-}05e^{3145.8(1/T)}$
3.75	Seawater	2.6E-03	12,903	$y = 0.0026e^{1552(1/T)}$
	Distilled Water	1.0E-11	65,628	$y = 1E\text{-}11e^{7893.7(1/T)}$
1	Seawater	5.0E-05	18,874	$y = 5E\text{-}05e^{2270.1(1/T)}$
	Distilled Water	9.0E-07	27,762	$y = 9E\text{-}07e^{3339.2(1/T)}$

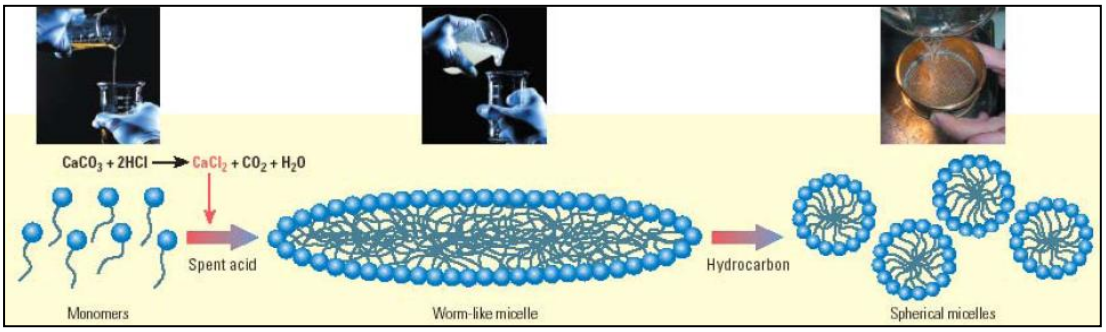

Figure 5.2.1: Illustration of VES structural changes due to acid spending and reaction with hydrocarbons. [Nasr-El-Din et al., 2008]

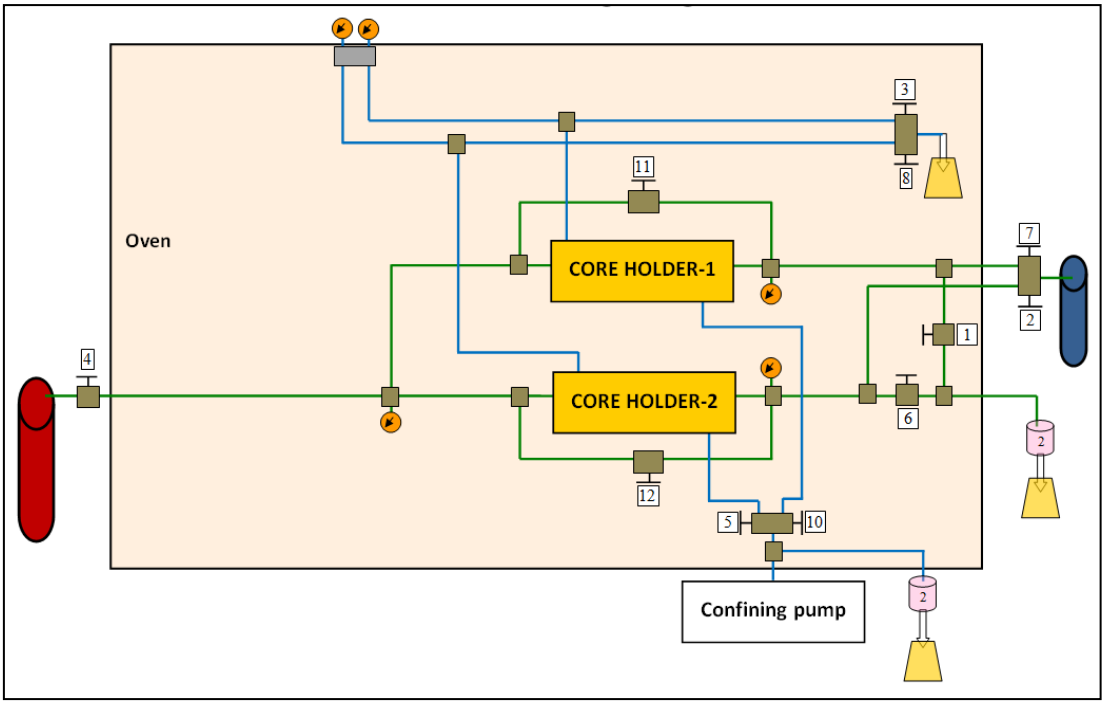

Figure 5.2.2: Schematic of the parallel core flooding apparatus.

Figure 5.2.3: Viscometer equipment.

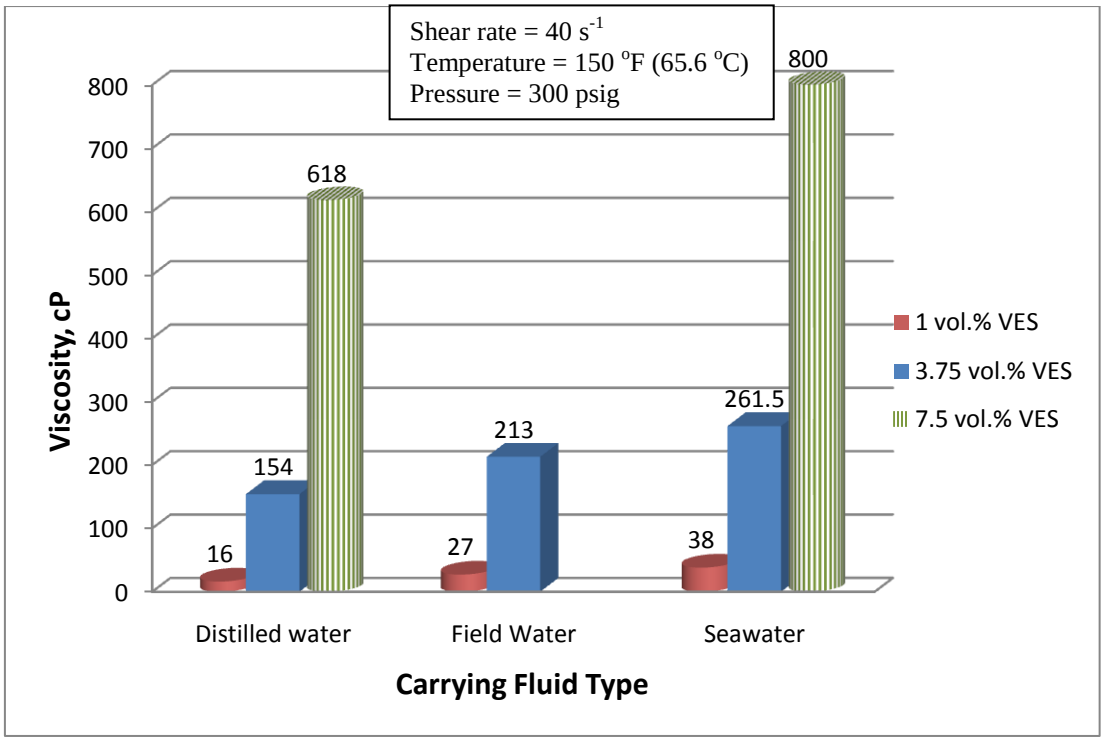

Figure 5.2.4: Salinity effect on the viscosity of spent acid solution containing different VES concentrations at 150 °F (65.6 °C).

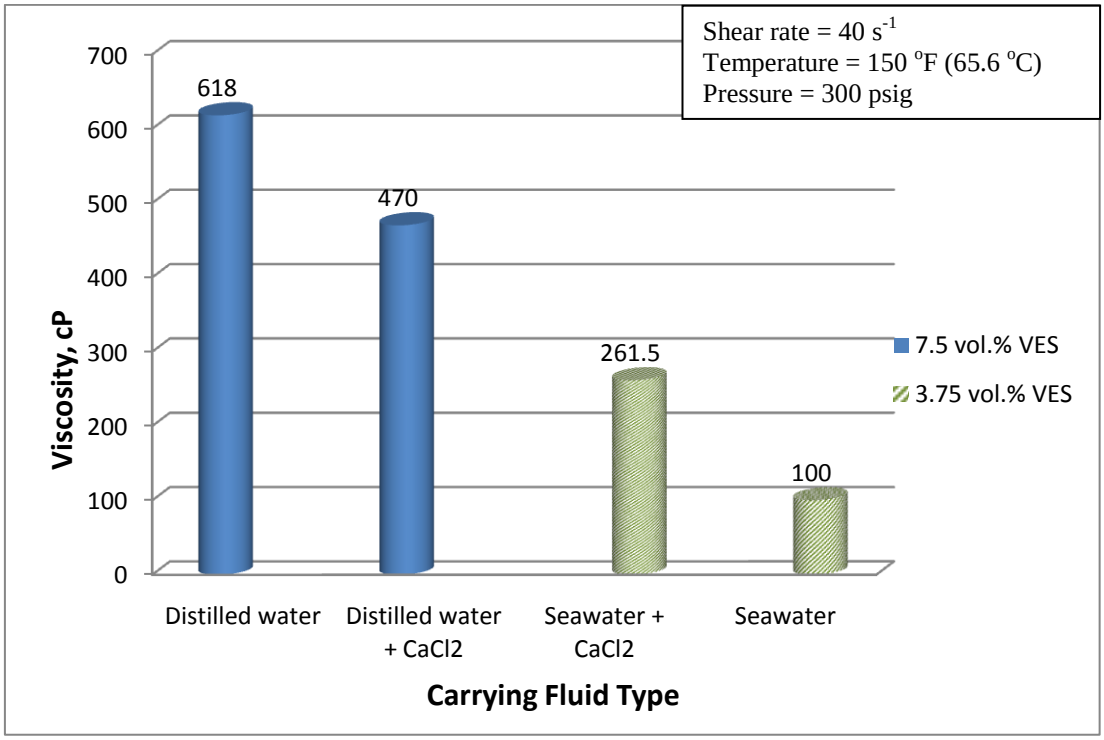

Figure 5.2.5: Effect of $CaCl_2$ on VES System Viscosity at 150 °F (65.6°C).

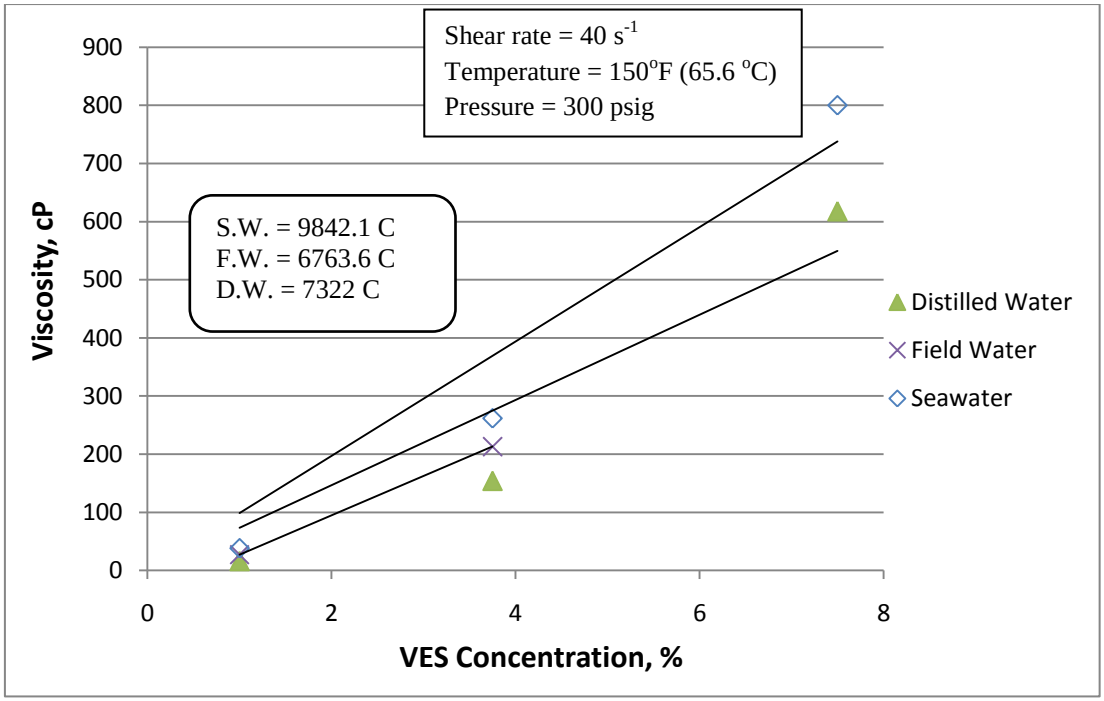

Figure 5.2.6: Effect of VES Concentration on spent acid VES system using different types of salinity at 150 °F (65.6°C).

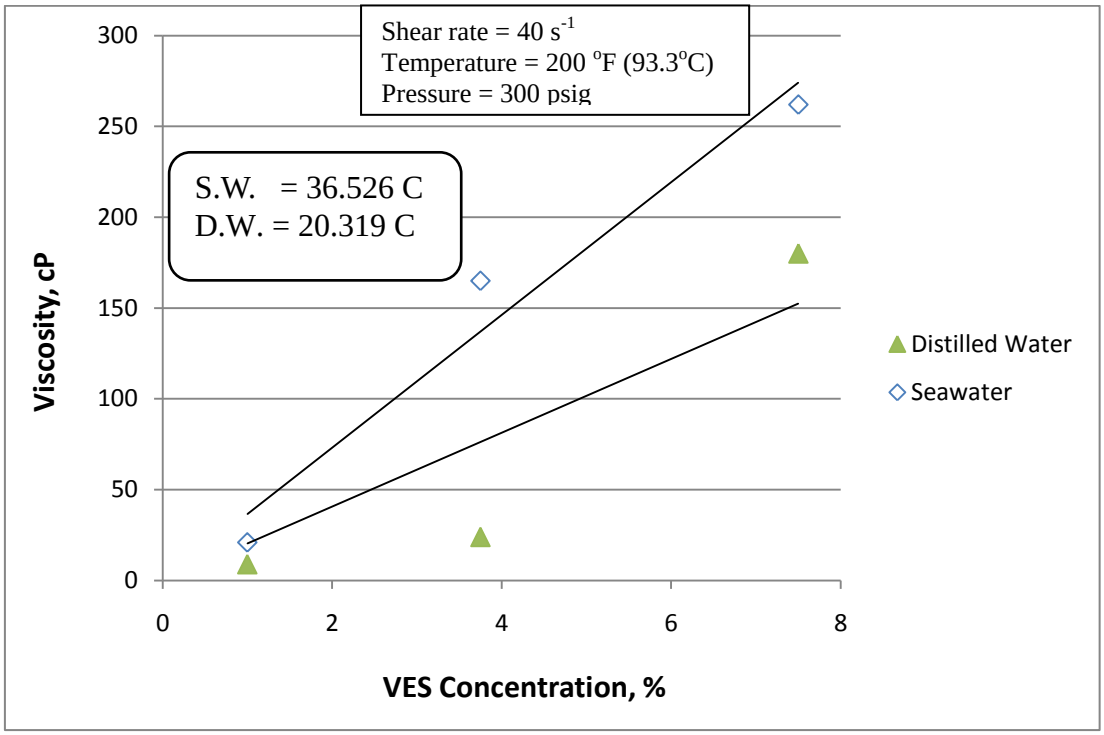

Figure 5.2.7: Effect of VES Concentration on spent 15% HCl VES system using varoius salinity mixing waters at 200 °F (93.3 °C).

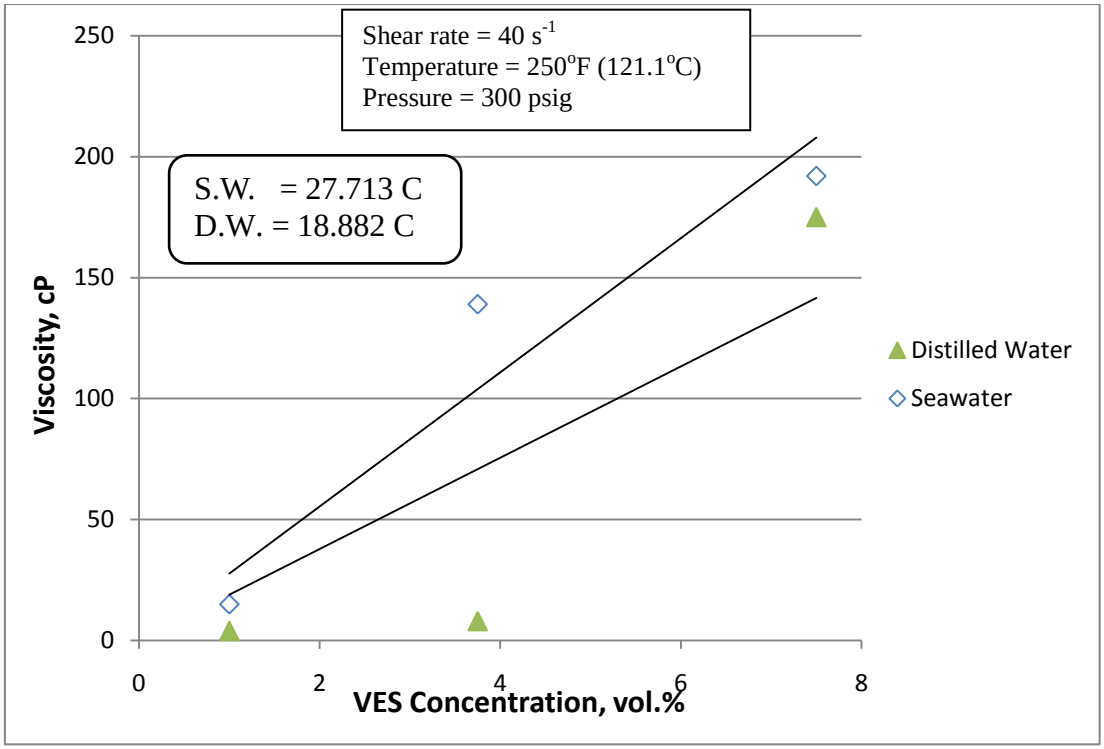

Figure 5.2.8: Effect of VES Concentration on spent acid VES system using varoius salinity mixing waters at 250 °F (121.1 °C).

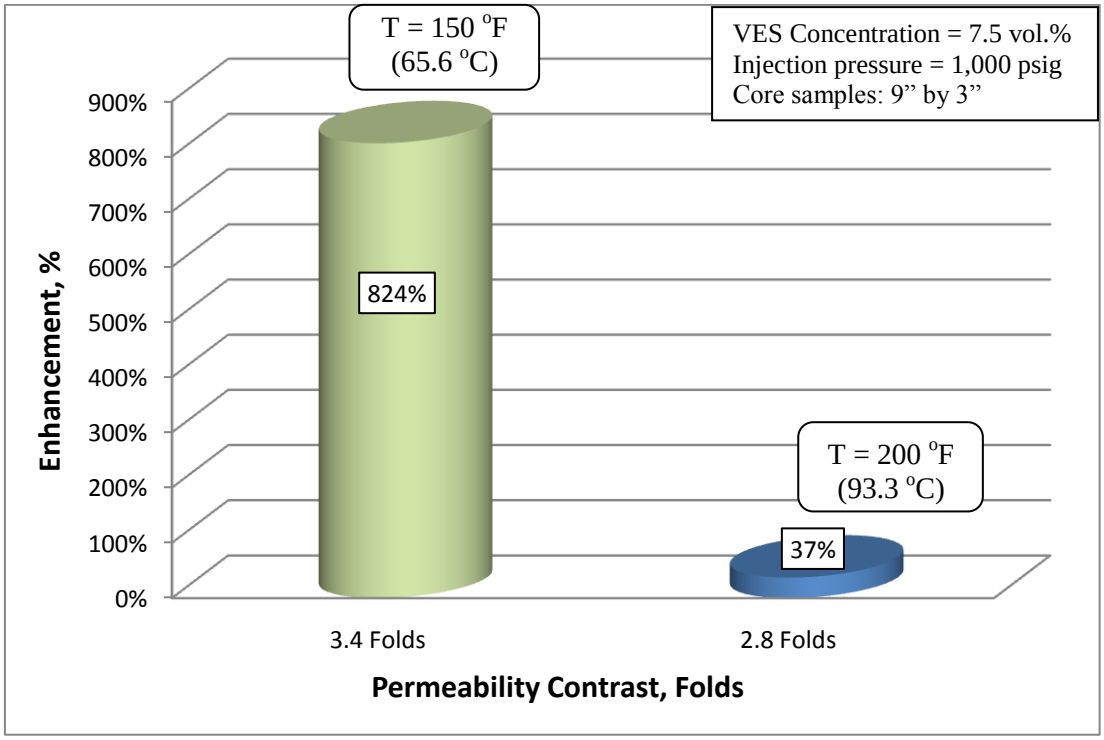

Figure 5.2.9: Effect of Temperature on the diversion efficiency of acid VES-based system using distilled water.

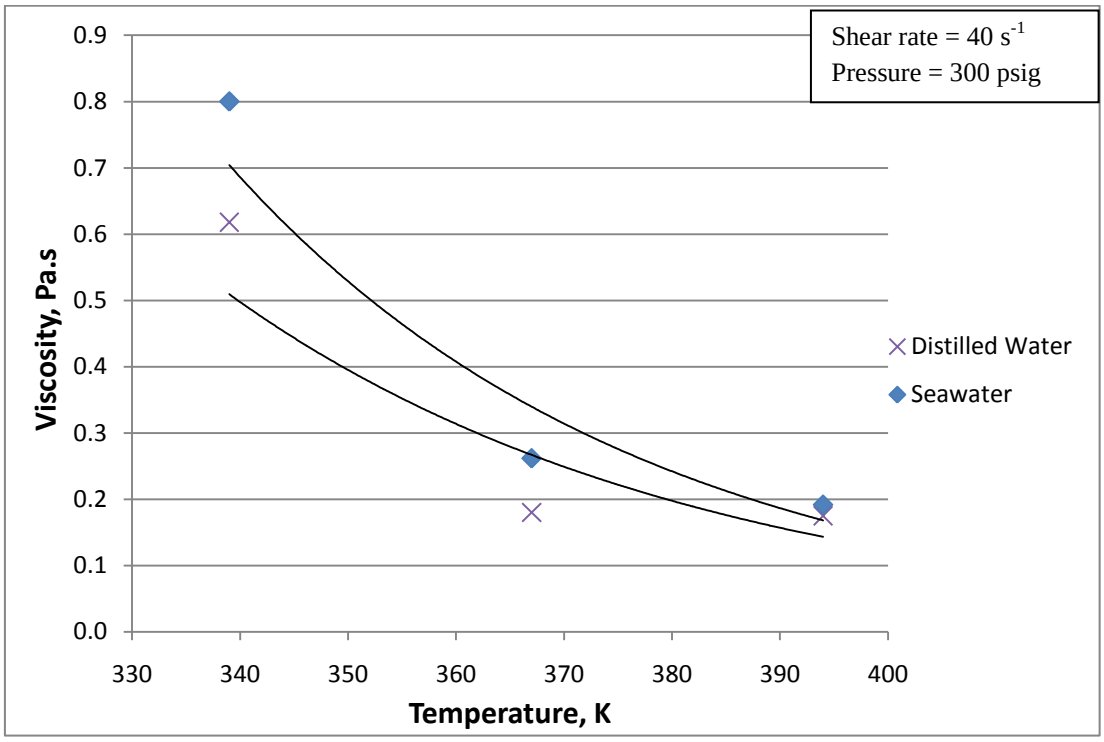

Figure 5.2.10-a: Effect of Temperature on the viscosity of spent acid with 7.5% VES.

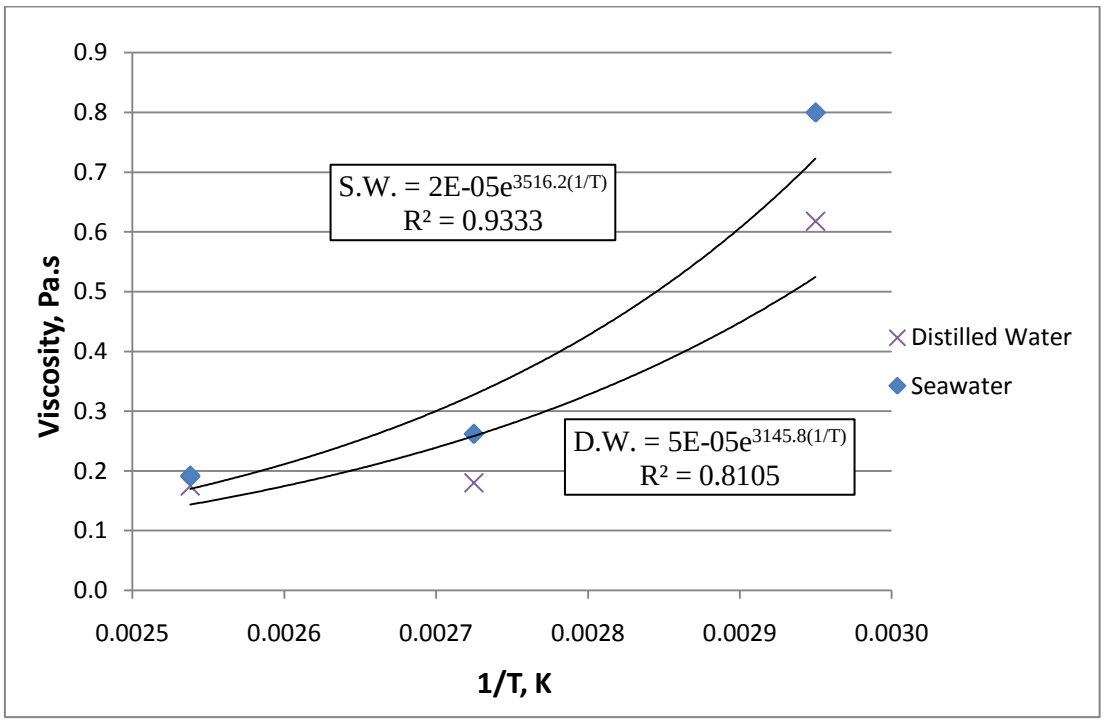

Figure 5.2.10-b: Effect of Temperature on the viscosity of spent acid with 7.5% VES $[y = A \times e^{E/RT}]$.

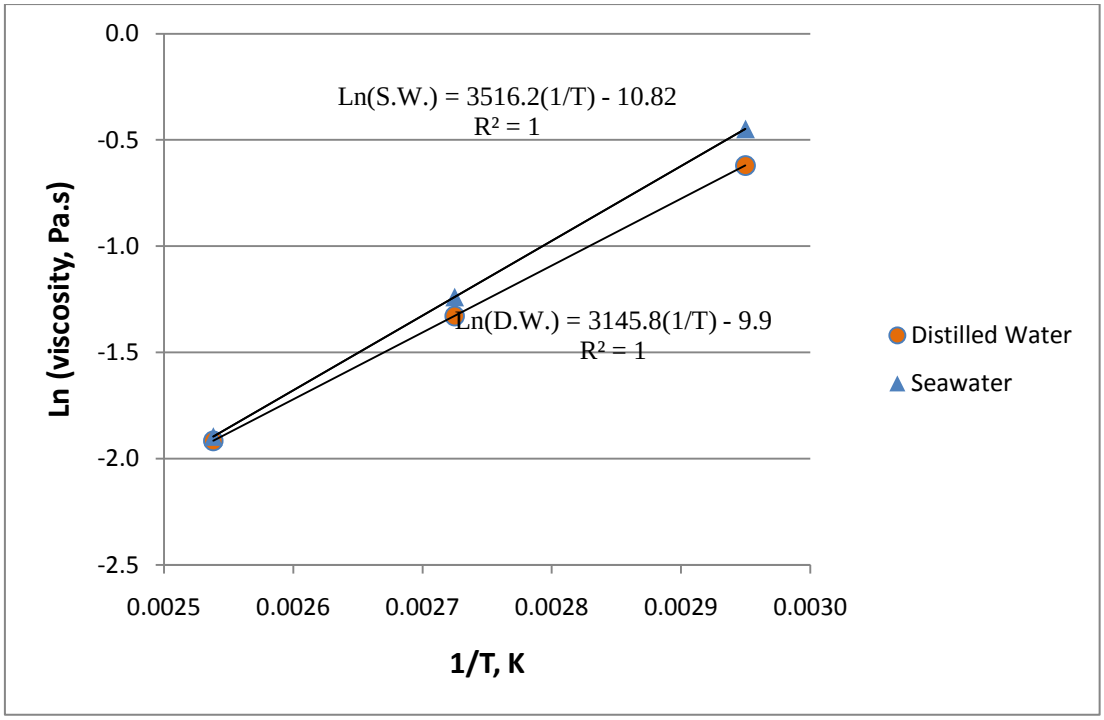

Figure 5.2.10-c: Effect of Temperature on the viscosity of spent acid containing 7.5% VES system [$Ln(y) = \frac{E}{RT} + Ln(A)$].

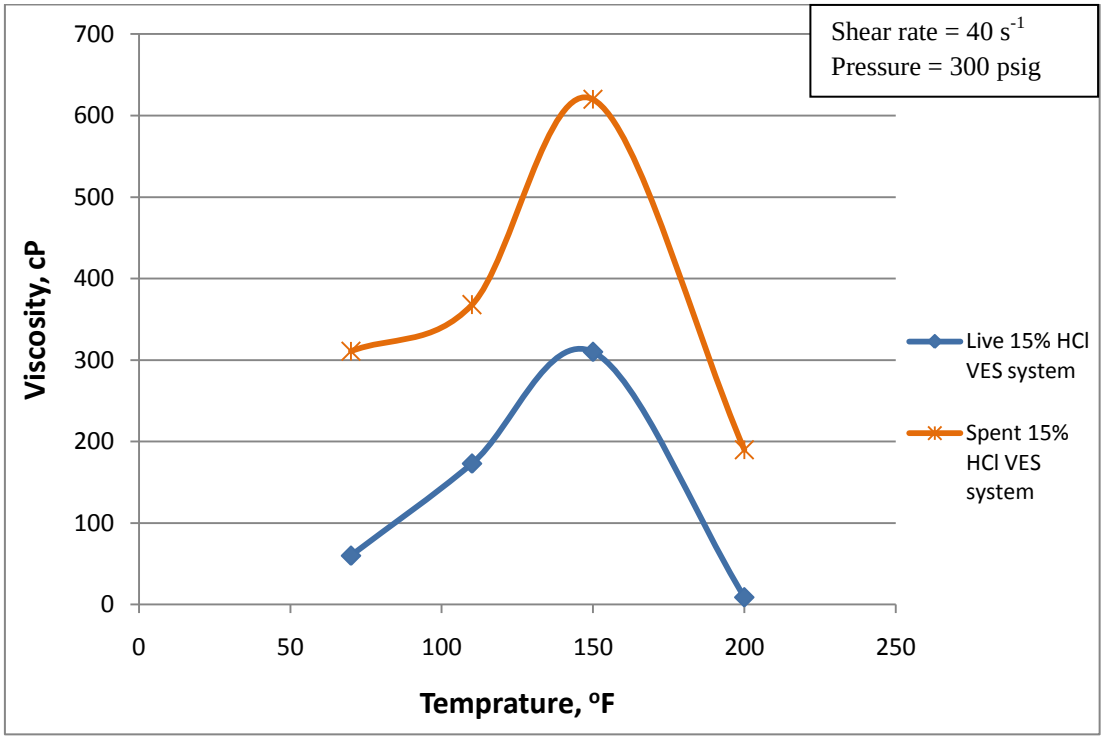

Figure 5.2.11: Effect of Temperature on the viscosity of live and spent acid containing 7.5% VES in distilled water.

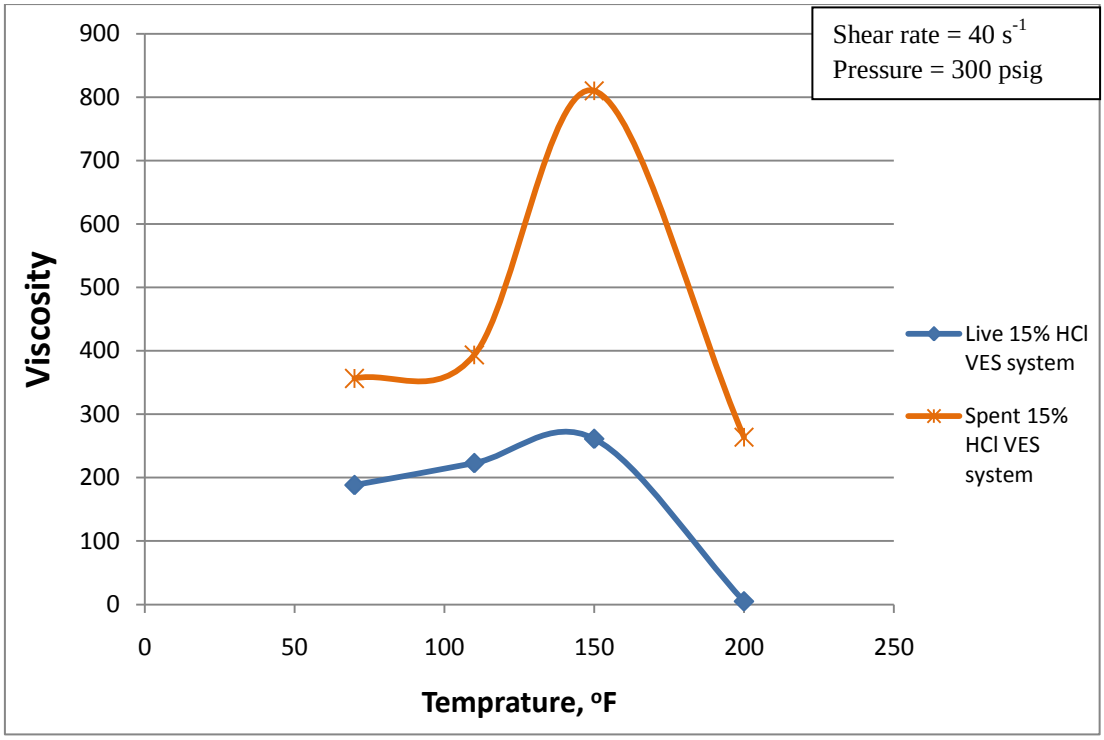

Figure 5.2.12: Effect of Temperature on the viscosity of live and spent acid containing 7.5% VES in seawater.

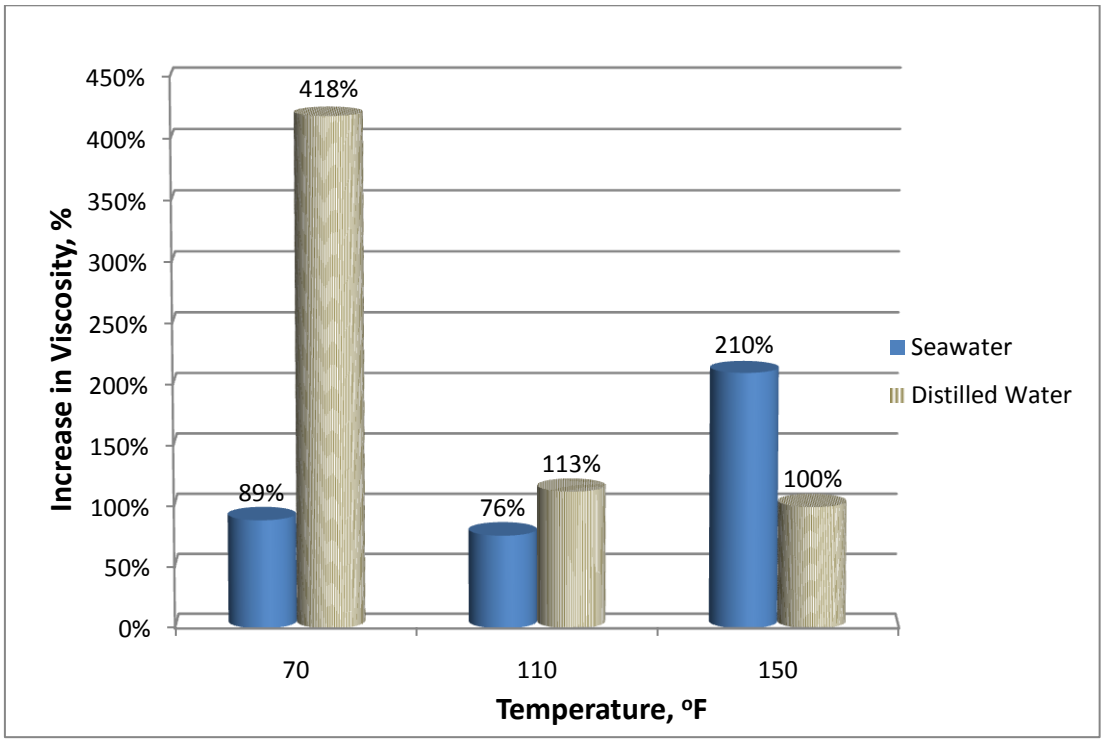

Figure 5.2.13: Viscosity increase percent as result of spending HCl acid containing 7.5 vol.% VES system

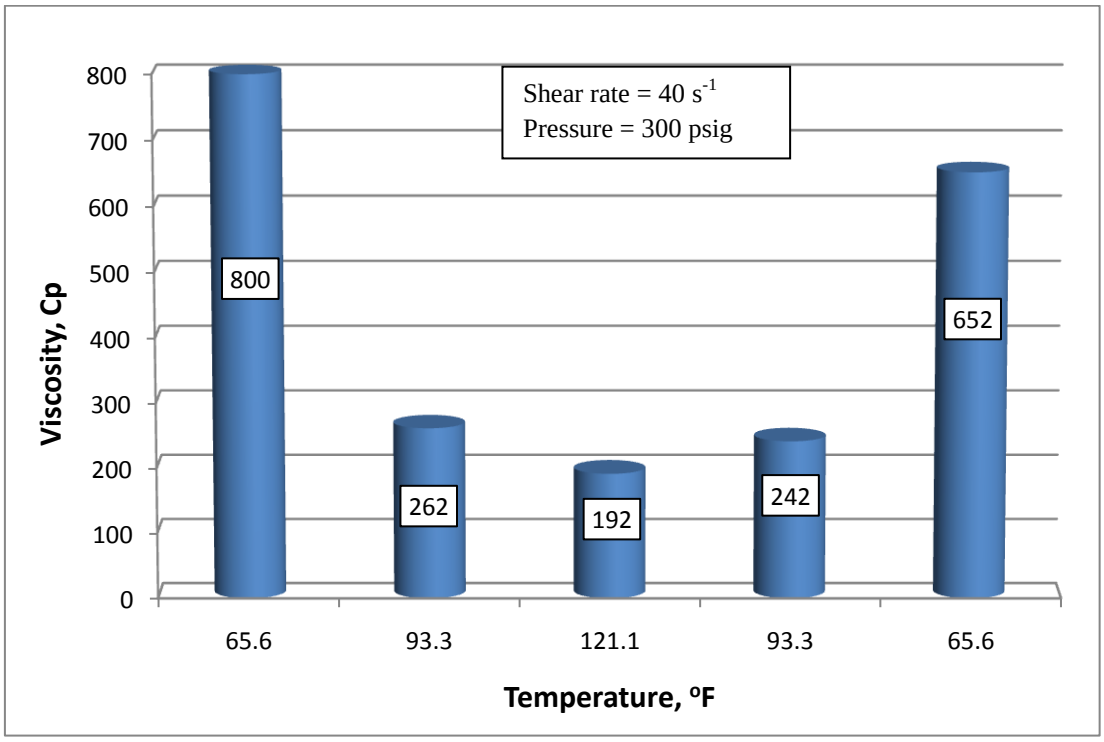

Figure 5.2.14: Thermal Stability of spent acid containing 7.5% VES system in seawater.

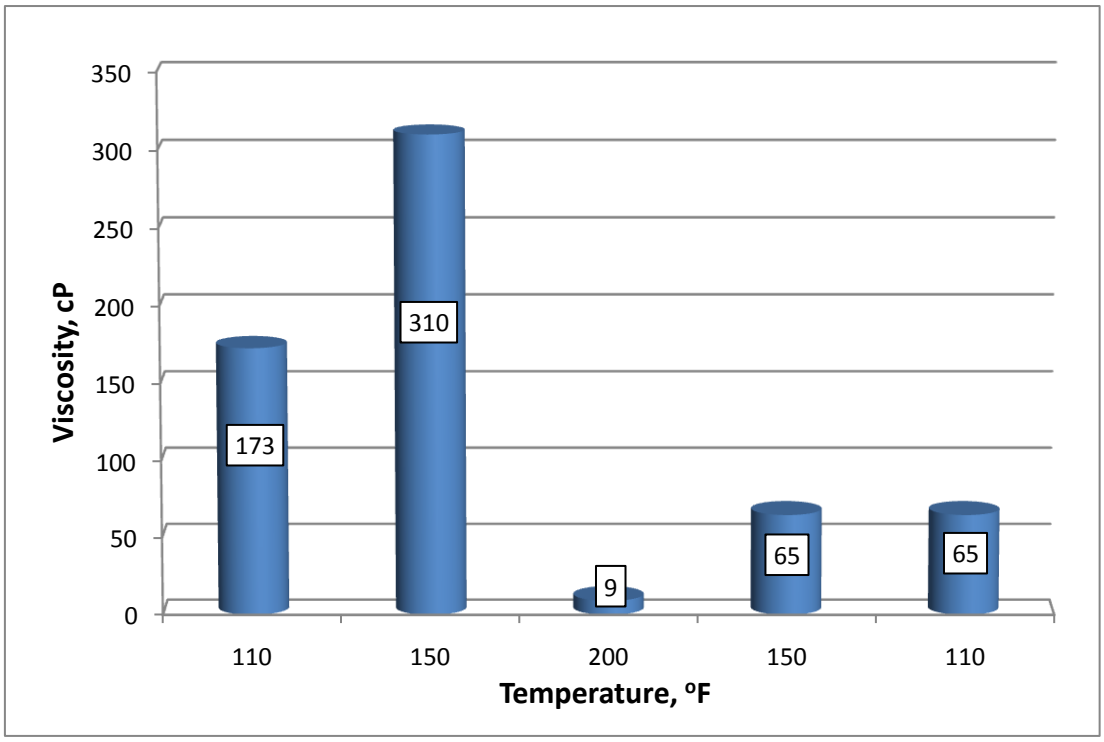

Figure 5.2.15: Thermal Stability of live acid with 7.5% VES in seawater.

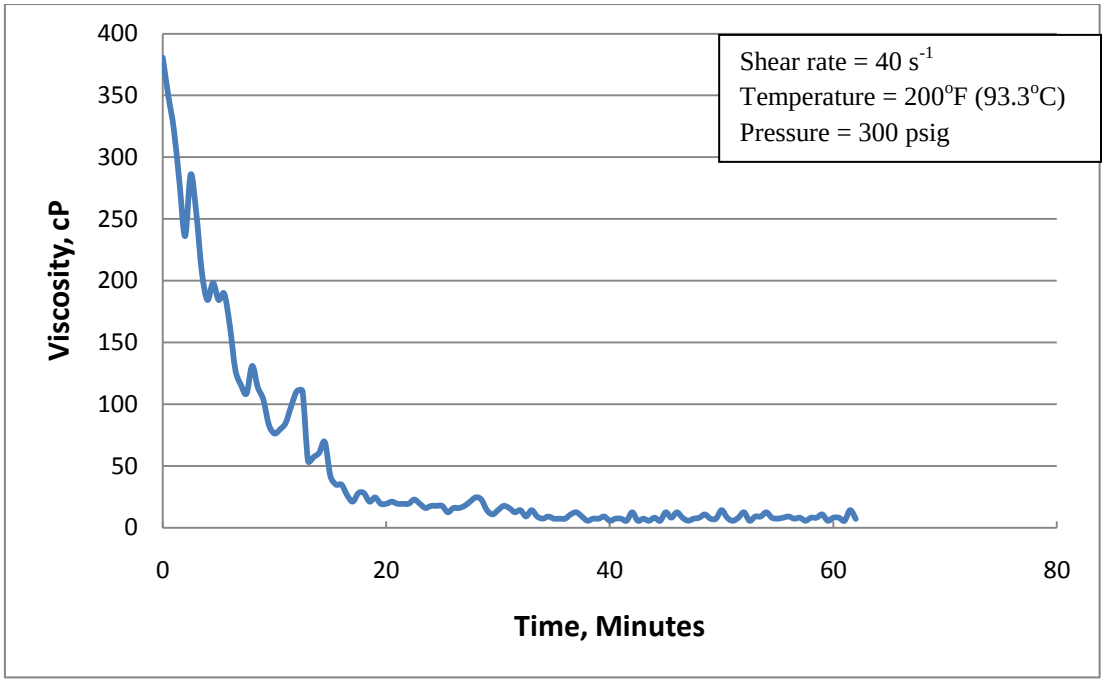

Figure 5.2.16: Temperature effect on the viscosity of live acid containing 7.5% VES system at 200 ^{o}F (93.3 ^{o}C) in distilled water.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

1. The acid VES based system has a significant impact on diverting HCl acid from higher permeability core samples to lower permeability cores samples.
2. The acid VES based system showed a diverting effect on HCl at high permeability contrasts of 80.5 folds.
3. The acid VES based system diversion efficiency was found to have an inverse relationship with the permeability contrast; the higher is the permeability contrast, the lower is the diversion efficiency of acid VES based system.
4. The concentration of VES showed a strong effect on the diversion efficiency; lowering the VES concentration resulted in lowering the diversion efficiency of the acid VES based system.
5. The salinity of the mixing water was found to be of a significant impact on the diversion efficiency of the acid VES based system; higher mixing waters salinity yielded higher diversion efficiency.
6. The mixing water salinity showed strong impact on the viscosity of spent 15% HCl acid VES based system.
7. Increasing the salinity of the mixing water from distilled water to seawater increased the viscosity by 30 – 69 % depending on the concentration of the VES.
8. $CaCl_2$ showed strong effect on increasing the viscosity of the VES system, proportional the concentration of the VES system (31.5% - 116%).
9. The viscosity of the spent 15% HCl VES based system was heavily dependent on

the concentration of the VES; it showed an increasing trend with concentration.

10. The temperature had a significant impact on both the viscosity of the VES system and diversion efficiency. The viscosity reduced from 800 to 192 CP when increasing the temperature from 150 ^{o}F (65.6 ^{o}C) to 250 ^{o}F (121.1 ^{o}C).
11. Increasing temperature from 150 ^{o}F (65.6 ^{o}C) to 200 ^{o}F (93.3 ^{o}C) reduced the diversion efficiency significantly from 824% to less than 37%.
12. Unusual increase in viscosity with temperature was observed in the range 80 ^{o}F (21.1 ^{o}C) - 150 ^{o}F (65.6 ^{o}C) for spent and live HCl acid VES based system.
13. Viscosity and diversion efficiency results imply that field application success rate of VES system is dependent on the targeted reservoir temperature.
14. Spending 15% HCl in VES system showed large increase in the viscosity of the VES based system ranging from 76% to 418% depending on the VES concentration and temperature.
15. Spent and live 15% HCl acid VES based system showed to be thermally unstable as it could not retain its original viscosity when heated at elevated temperatures.
16. Optimization of the target solution viscosity can be obtained by using high salinity water and lower VES concentration.

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